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BREAK JUNCTIONS I

Interim Report

October 1, 1986 to September 31, 1987

**John Moreland, L. F. Goodrich, J. W. Ekin, T. E. Capobianco,
and A. F. Clark**

Electromagnetic Technology Division
Center for Electronics and Electrical Engineering
National Engineering Laboratory
National Bureau of Standards
U.S. Department of Commerce
Boulder, Colorado 80303-3328

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U.S. DEPARTMENT OF COMMERCE, C. William Verity, Secretary

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

FOREWORD

This report summarizes the work performed during FY 87 by the Superconductor and Magnetic Measurements Group at the National Bureau of Standards using break junctions for tunneling spectroscopy of superconductors. It is intended not only as an NBSIR but as the FY 87 interim report to ONR as well, since the work was primarily funded by the Office of Naval Research.

Break junctions belong to a relatively new class of tunneling junctions that rely on the spacing of two conductors with a one-nanometer vacuum, gas, or liquid insulator. As the name "break junction" implies, this is done within the fracture of a conducting material permitting tunneling spectroscopy of freshly exposed bulk surfaces. As is the case for all vacuum tunneling techniques, this eliminates the need for thin-film depositions of samples or tunneling barriers traditionally employed in tunneling experiments. The break junction technique is a result of recent developments at NBS on methods for measuring the superconducting properties of bulk materials. Primarily our efforts have centered around multifilamentary superconductors for magnets to be used for fusion, superconducting accelerators, and magnetic resonance imaging. In particular, the break junction method was first used for measuring the energy gap of Nb-Sn and Nb-Ti filaments extracted from the matrix of a multifilamentary superconductor.

In this report we discuss recent improvements in the break junction method and its uses for studying some of the more exotic superconducting materials. Tunneling measurements of the superconducting energy gap function and Josephson effect in the high-T_c materials $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_x$ are presented.

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BREAK JUNCTIONS I

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October 1, 1986 to September 31, 1987

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Measurements of the tunneling current-voltage characteristics of break junctions in conventional superconductors can be used to determine their superconducting energy gap as a function of energy. These results agree with those previously obtained using traditional oxide tunneling barriers. Break junctions in some exotic superconductors, on the other hand, have anomalous current-voltage characteristics compared to BCS predictions. Energy gaps and the Josephson effect measured for the new high T_c materials YBaCuO ($T_c = 93$ K) and LaSrCuO ($T_c = 36$ K) indicate that the samples are inhomogeneous with varying gap functions depending on the location of the tunneling contact within the break junction fracture. Break junction data for these materials are within the strong coupling limits of BCS theory.

Key words: break junctions; electron tunneling; energy gap; high- T_c superconductors; LaSrCuO; YBaCuO; YBa₂Cu₃O_{7- δ}

INTRODUCTION

Electron tunneling has many uses in the field of materials science. We begin with a short descriptive bibliography. There are several texts summarizing developments over the last thirty years related to electron tunneling phenomena. General overviews by Duke, [1] Hansma, [2] and Burstein and Lundqvist [3] outline various applications of the tunneling phenomena to metals, semiconductors, superconductors, and surface adsorbates.

Electron tunneling between superconductors, in particular, is also reviewed by several authors. Some introductions to tunneling spectroscopy and the Josephson effect are presented by Scalapino and Rowell and McMillan in Parks. [4] Wolf [5] reviews some of the recent developments in tunneling spectroscopy of superconductors including the proximity effect and its effect on tunneling spectra and the superconductive energy gap function derived from tunneling data.

The works mentioned above are mostly based on tunneling junctions fabricated using a thin oxide tunneling barrier. The development of vacuum tunneling methods has extended the uses of tunneling to include scanning capabilities with atomic topographic resolution. The scanning tunneling microscope invented by Binnig and Rohrer is reviewed in two volumes of the IBM Journal of Research and Development. [6]

Recently application of vacuum tunneling junctions has been extended to spectroscopy. In particular, the squeezable electron tunneling (SET) junction invented by Hansma, Moreland, and Alexander [7] has been used to study semiconductor band gaps and superconductor energy gaps. SET junctions offer ultra-stable electromechanical systems for tunneling spectroscopy. Break junctions were developed at NBS by Moreland, Ekin, and Clark [8] to study superconductors in their native state without using thin film depositions normally required for tunneling experiments. Both SET junctions and break junctions have sufficient mechanical stability for measuring the superconducting energy gaps. The patent application reproduced in the appendix gives a detailed description of the break junction technique.

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ELECTRON TUNNELING MEASUREMENT OF THE ENERGY GAP
IN A La-Sr-Cu-O SUPERCONDUCTOR[†]

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The break junction technique has been used to determine the energy gap of lanthanum-strontium-copper-oxide, one of the new high critical temperature superconductors. The current-voltage characteristics demonstrated a variety of tunneling behaviors. The best characteristic indicating quasiparticle tunneling between superconducting electrodes implied an energy gap of $7.0 \text{ meV} \pm 0.1 \text{ meV}$. Derivatives of other characteristics showed weak structure indicating possible energy gaps up to 9 meV.

The break junction technique [1] has been used to determine the energy gap of lanthanum-strontium-copper-oxide, one of the new high critical temperature superconductors. [2] In this technique, a small piece of bulk material is electromechanically fractured under liquid helium and the freshly fractured surfaces adjusted to form a tunneling barrier with the helium as the insulator. Extraordinarily precise mechanical adjustment permits the study of electron tunneling phenomena between pieces of a bulk superconductor.

The material measured was a sintered metal powder ceramic manufactured at the Ames Laboratory [3] and had the chemical form $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. It had an onset critical temperature, T_c , of 36 K as determined from ac susceptibility measurements. The pellet was cut with a diamond saw to provide small rods (1 mm x 1 mm x 10 mm) for the break junction technique.

Preliminary results of this experiment are shown in Figure 1. The current-voltage (I-V) characteristics in the figure demonstrate some of the variety of the observed tunneling behavior for the various settings of the tunneling barrier spanning the break. The uppermost I-V curve indicates quasiparticle tunneling between superconducting electrodes. [4] The gap-sum voltage is 28

[†] Published in *Cryogenics* 27, 227 (1987).

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mV \pm 0.5 mV. The gap-sum voltage equals four times the superconductive energy gap, Δ/e , assuming identical material on either side of the break. This implies that $\Delta = 7.0 \text{ meV} \pm 0.1 \text{ meV}$, which is consistent with the high T_C of this material. (The Δ for Nb_3Sn , for example, is 3.4 meV for a T_C of 18 K.) This I-V curve occurred only once during many adjustments of the junction. The middle I-V curve occurred more often. Notice the increased deviation from antisymmetry and the washed out gap. Derivatives of these types of I-V curves showed weak structure indicating possible gap-sum voltages as high as 35 mV, with corresponding energy gaps of about 9 meV. For these values of the energy gap and the onset T_C , the ratio $2\Delta/k_B T_C$ ranges from 4.5 to 5.8 as compared to the BCS value of 3.4.

By far, the most common I-V characteristic was of the type shown at the bottom of Figure 1. These characteristics showed very little structure even in derivative traces and appeared to closely follow a quadratic current dependence on voltage.

Scanning electron microscope pictures of the fracture surfaces between which the tunneling occurs show a rough surface with frequent voids and scattered inclusions. It is probable that tunneling shifts from point to point and thus occurs between different phases of the material. The variability in the tunneling I-V curves may thus be due to tunneling between materials with different energy gaps and also perhaps across non-superconducting material as well.

ACKNOWLEDGEMENTS

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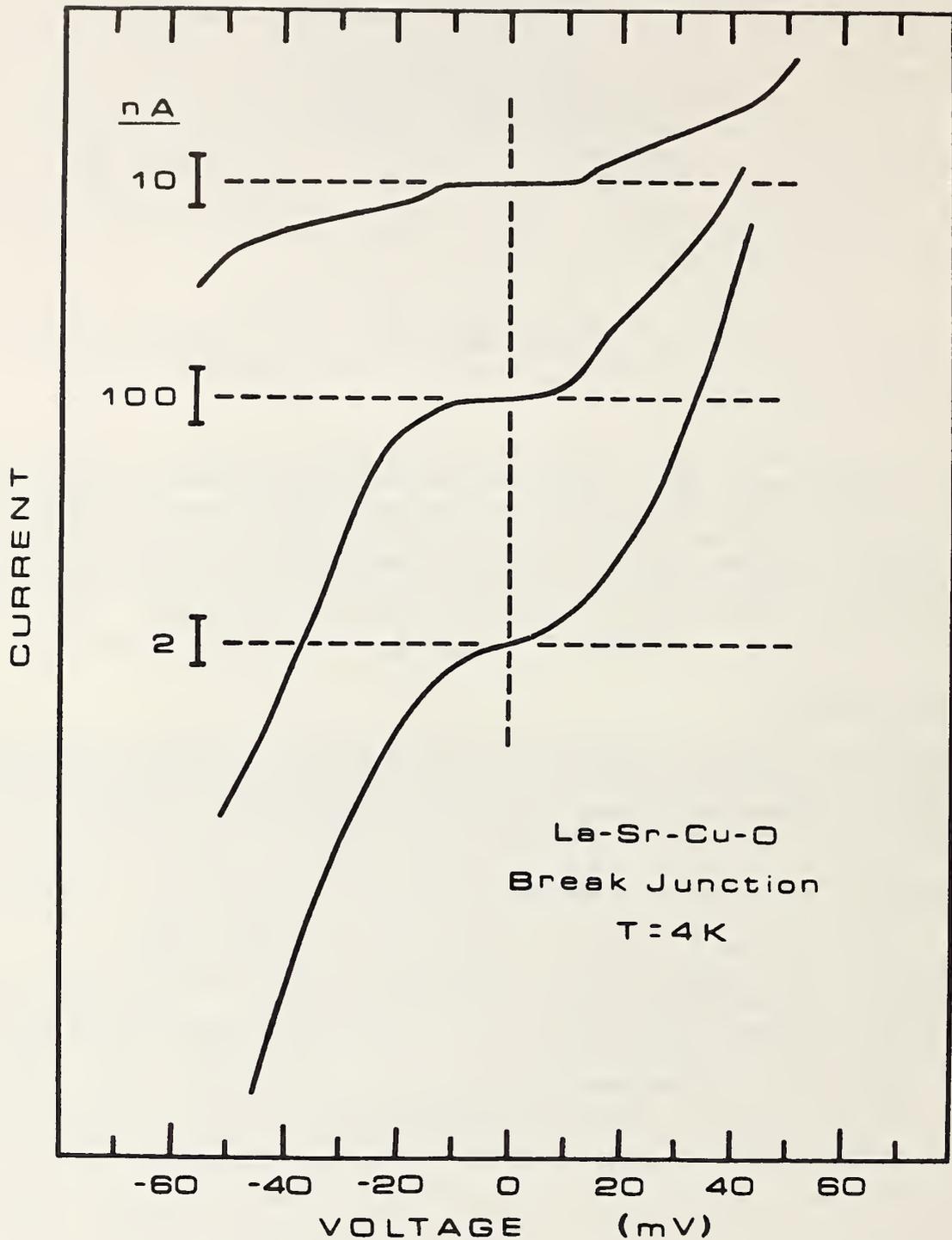


Fig 1. Current-voltage curves of a La-Sr-Cu-O electron tunneling break junction immersed in liquid helium at 4 K. The curves demonstrate the types of tunneling characteristics obtained at different break junction barrier settings. The junction resistance measured at +20 mV was 5 M Ω for the upper curve, 170 K Ω for the middle curve, and 8 M Ω for the lower curve.

TUNNELING SPECTROSCOPY OF A La-Sr-Cu-O BREAK JUNCTION: EVIDENCE FOR
STRONG-COUPPLING SUPERCONDUCTIVITY[†]

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Detailed structure in the quasiparticle tunneling has been observed in La-Sr-Cu-O superconductive tunneling junctions using the break junction technique. Variability in the energy gap and associated structure in the current-voltage curves is observed indicating significant inhomogeneity in the superconducting properties. Large energy gaps (7.0 - 9.0 meV) and deep structure in the conductance derivatives are evidence for a strong coupling mechanism.

Quasiparticle tunneling has been observed in La-Sr-Cu-O superconductive tunneling junctions. [1-5] These measurements were on samples with onset superconductive transition temperatures of $T_c = 36$ K to 35 K. The corresponding superconductive energy gaps determined from the measured I-V characteristics ranged from $\Delta = 7$ meV to 14 meV. This implies strong coupling superconductivity in La-Sr-Cu-O since $2\Delta/k_B T_c$ ranges from 4.5 to 9.0 compared to the BCS prediction of 3.4.⁶

Break junction tunneling experiments, in particular, have the potential for providing some of the most informative details of the quasiparticle states in the new high T_c materials. This is because tunneling occurs across the fracture of a bulk sample. [1,7] That sample may be a single crystal, polycrystal, or sintered pellet.

In this paper, we present additional evidence for strong coupling in La-Sr-Cu-O. Derivatives of the I-V characteristics show that the quasiparticle tunneling conductance of a La-Sr-Cu-O break junction can vary as much as 30% over voltages ranging from the gap edge at $2\Delta/e$ to 50 mV. These variations are large compared to those observed in superconductive-Pb tunneling junctions, for example, where strong electron-phonon coupling causes up to 4% conductance deviations from the theoretical BCS density of states.

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The material measured was a sintered metal powdered ceramic with the chemical form $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. It had an onset T_c of 36 K as determined from ac susceptibility measurements. [8] The pellet was cut with a diamond saw into small rods (1 x 1 x 10 mm) for the break junction technique. All measurements were performed using a break junction apparatus designed for dipping in liquid helium storage dewars ($T = 4$ K). The junction actuator was an electromagnet of the type described by Moreland and Hansma. [9] We measured the magnetic field in the vicinity of the junctions and found it to be less than a few gauss. First derivatives of the I-V curves were taken using the standard lock-in technique with a modulation voltage of 420 μV .

As discussed in a previous paper [1] these junctions must be adjusted (mechanically set and reset) many times to obtain I-V characteristics indicative of quasiparticle tunneling. We believe this phenomenon is due to sample inhomogeneity since break junction measurements on pure Pb and Sn indicate low leakage quasiparticle tunneling independent of junction setting. As a junction is set and reset tunneling probably shifts between different points within the fracture, thus sampling different materials. Alternatively, with continued adjustment, the surface of the fracture elements may have been worn away exposing subsurface superconductor. The former conjecture is supported by SEM micrographs of the fractured surfaces examined after the junction I-V measurements. The fractured surfaces show scattered inclusions and voids down to less than 0.1 μm scales. The latter possibility is supported by TEM micrographs [10] showing lattice distortion at the grain boundaries of these materials that may destroy conductivity as well as superconductivity.

Figure 1a shows the predominate type of I-V characteristic observed during adjustments of the junctions. These characteristics showed very little structure and appeared to closely follow a quadratic current dependence on voltage. Zeller and Giaever [11] attribute this kind of tunneling behavior to the granular nature of a superconductor with insulating intergrain regions. A model based on the remnant voltage caused by itinerant electrons residing on individual capacitive grains agreed well with their measurements on Sn particles. They found that when the Sn particles were normal and less than 20 nm in diameter, the junction conductance increased linearly with bias giving rise to a zero bias resistance anomaly similar to that in figure 1a. When the particles were superconducting, a step near the peak in the superconducting density of states occurred in the conductance curves with finite conductance at zero bias. This behavior has also been observed in La-Sr-Cu-O break junctions [1] as well as point contact [4,5] and scanning tunneling microscopy experiments. [2,3] Another tantalizing observation made by Zeller and Giaever was that the experimental T_c 's of the small Sn particles were elevated from the bulk value.

The granular model, when applied to La-Sr-Cu-O, may be discrepant in that the 1 μm grain size measured in these materials is much larger than the 20 nm in the study by Zeller and Giaever. However, as Kirtley et al. [2] point out, the grain size may not be appropriate for comparison. Perhaps stoichiometric variations (La versus Sr) preserve the crystal lattice but not local superconductivity. Natural granularity provided by the layered perovskite structure of La-Sr-Cu-O may be another possibility.

Occasionally our break junction settings would result in I-V traces with the more familiar quasiparticle current curve. The results for one particularly interesting setting are shown in figure 1b. Notice the sloping curve indicating that at least one of the electrodes has the granular nature discussed above, and the presence of a superconducting energy gap near zero bias spanning the voltage range from -7 mV to 7 mV. Assuming identical material on either side of the junction then $4\Delta/e = 14$ mV or $\Delta = 3.5$ meV. However, since previous measurements have resulted in higher gap values (7 meV or larger) perhaps the proper assumption would be that one side of the junction is granular normal with the other side having a full superconductive energy gap value of 7 meV. Since this is more consistent with the current picture we will assume SIN tunneling in what follows.

Figure 2 shows the first derivative (dynamic conductance) of figure 1b. Notice the central conductance minimum corresponding to the tunneling energy gap flanked by symmetric maxima and minima as a function of voltage. We estimate the normal conductance of the junction to be around $0.60 \mu\text{mhos}$ and the structure to be 30% to 40% variations about this value. This compares with measurements on Al-Al₂O₃-Pb junctions (Al normal) where conductance variations outside of the gap reach only 4% of that in the normal state. [12] Since Pb is a well known strong coupling superconductor, this implies a very strong coupling mechanism in La-Cu-Sr-O.

Figure 3 shows the second derivative (d^2V/dI^2) of figure 1b. This curve was digitally generated from figure 2 which was used as input into the McMillan-Rowell computer program [13] for calculating $\alpha^2F(\omega)$, the frequency dependent coupling parameter derived from tunneling conductance data. Generally, extrema in the second derivative indicate coupling of tunneling electrons to the normal modes of the materials comprising the junction. Some of these modes may be responsible for the high T_c superconductivity in these compounds. For example, preliminary analysis of this data using the McMillan-Rowell program indicate that possible low energy phonon modes apparent in the second derivative curve near 5 and 15 mV from the gap edge could very well account for the high T_c of this material. This is assuming an ohmic normal state conductance of $60 \mu\text{mhos}$. We caution, however, that our present apparatus could not be used to measure the true normal state conductance of the break junction. In addition, the sloping I-V curves made it difficult to accurately estimate the normal state conductance. Since a normal state measurement is required to accurately calculate phonon couplings, any resulting theoretical T_c would be suspect.

The data presented here represents some of our "best" results in that the curves are close to being symmetric about zero bias. The majority of our data showed a great deal of variability with a lot of detailed structure in the curves. All indications lead to the conclusion that we have more to learn about the superconductivity in these materials, in particular, what is the role of sample inhomogeneity.

ACKNOWLEDGEMENTS

This work was supported at NBS by the Office of Naval Research, Grant #N00014-86-F-0109. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. The authors wish to thank K. E. Kilhstrom, Westmont College, Santa Barbara, California for supplying us with the McMillan-Rowell program.

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La-Sr-Cu-O
4 K

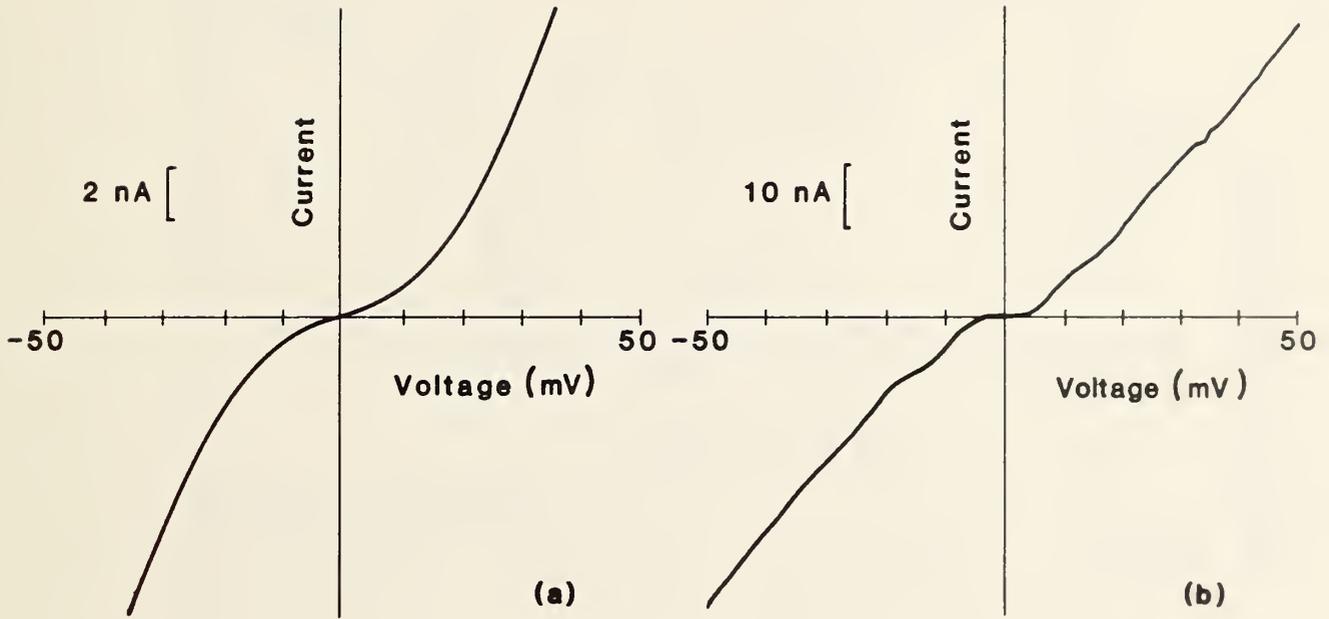


Fig 1. I-V characteristics of a La-Sr-Cu-O break junction immersed in liquid helium at 4 K.

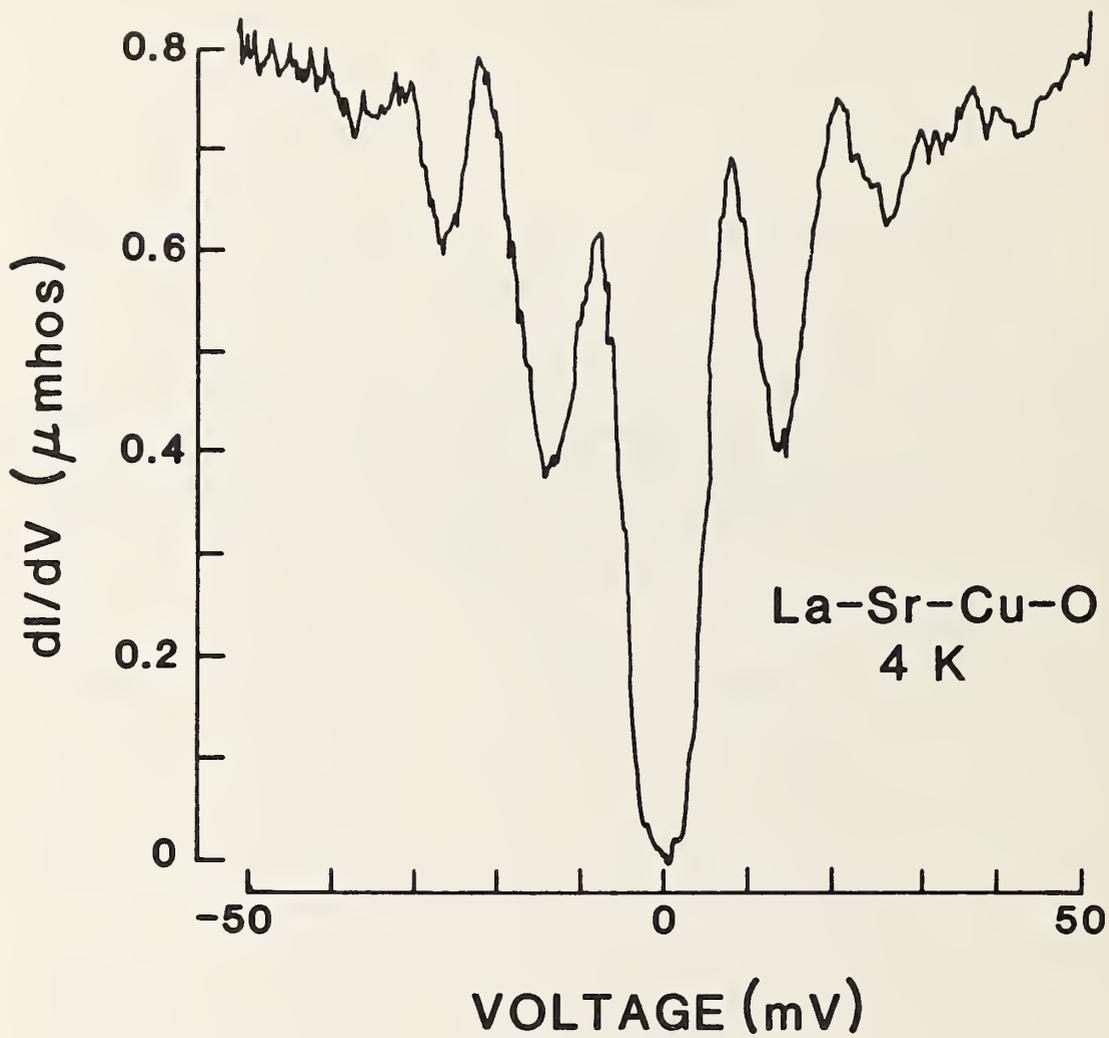


Fig. 2. dI/dV vs. V for figure 1b.

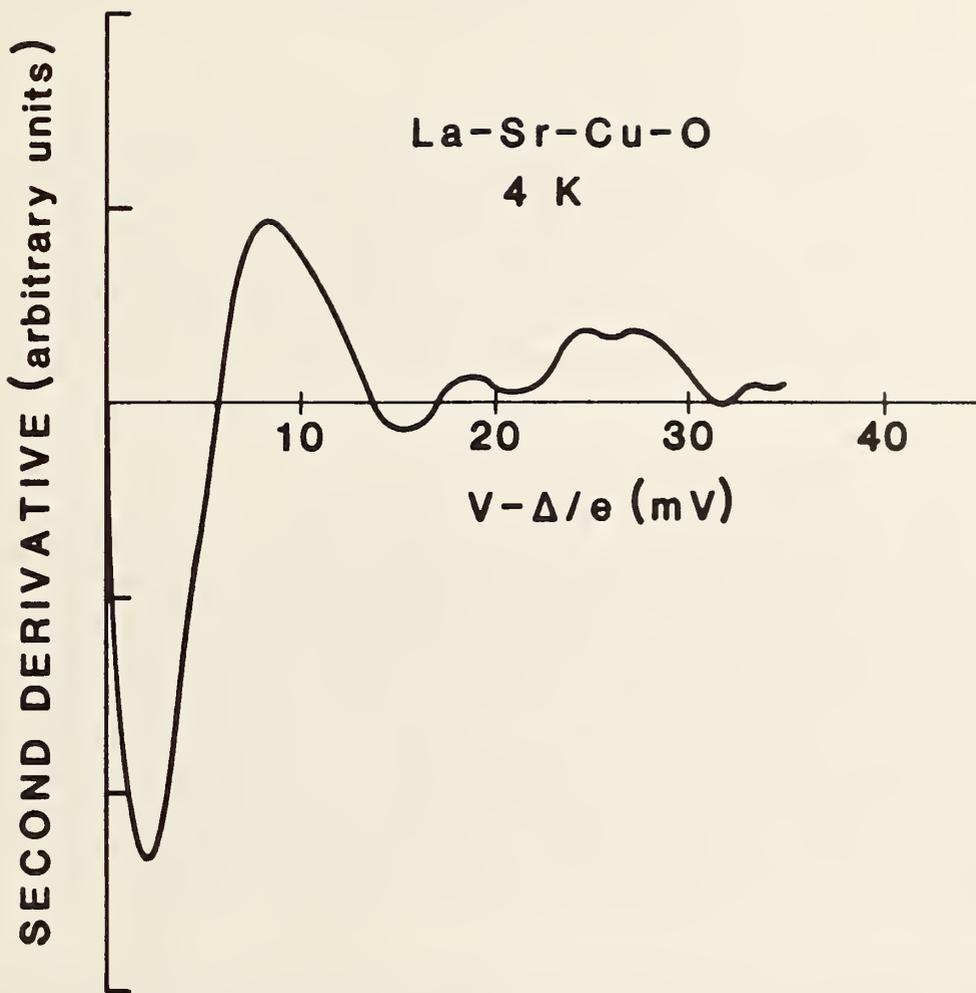


Fig. 3. d^2V/dI^2 vs. $V - \Delta/e$ for figure 2.

BREAK-JUNCTION TUNNELING MEASUREMENTS OF THE HIGH- T_C SUPERCONDUCTOR
 $Y_1Ba_2Cu_3O_{9-\delta}$ [†]

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Current-voltage tunneling characteristics in a high critical-temperature superconducting material containing predominately $Y_1Ba_2Cu_3O_{9-\delta}$ have been measured using the break junction technique. Sharp gap structure was observed, with the largest superconductive energy gap measured to be $\Delta = 19.5 \text{ meV} \pm 1 \text{ meV}$, assuming a superconductor-insulator-superconductor junction. This energy gap corresponds to $2\Delta/k_B T_C = 4.8$ at $T = 4 \text{ K}$, for a critical temperature of 93 K (mid-point of the resistive transition).

Since the discovery of high critical-temperature ($T_C \approx 90 \text{ K}$) superconductivity in the Y-Ba-Cu-O system, [1] a number of experimental techniques have been used to study these new superconducting compounds. This letter reports tunneling measurements in this high T_C superconductor using the relatively new break-junction technique. [2] These measurements were made on a bulk sample with the predominant superconducting phase $Y_1Ba_2Cu_3O_{9-\delta}$ (where δ indicates an undetermined amount of oxygen deficiency), with T_C onset at 95 K and $R = 0$ at 91 K. Variations of the energy gap, Δ , along with the gap structure were observed as the junction was set and reset; the largest energy gap was $19.5 \text{ meV} \pm 1 \text{ meV}$. For a critical temperature of 93K (mid-point of the resistive transition), [3,4] this value of the energy gap corresponds to $2\Delta/k_B T_C = 4.8$, which is larger than would be expected from the BCS prediction of $2\Delta/k_B T_C = 3.5$. This value is consistent with strongly coupled superconductors.

The break-junction technique used in this study has the potential for providing details of the quasiparticle states in the new high T_C materials. In a break junction, tunneling occurs across the fracture of a bulk sample. A small piece of bulk material is electromechanically fractured under liquid helium, and the freshly fractured surfaces are adjusted to form a tunneling barrier with the helium as the insulator. A break-junction sample may be a single crystal, polycrystal, or sintered pellet. The break-junction method

[†] Published in Phys. Rev. B 35, 8856 (1987).

has been useful in providing tunneling data in the La-Sr-Cu-O superconductor system, [5,6] along with other tunneling studies using the point contact technique [7,8] and the scanning tunneling microscope. [9,10] Unlike these other tunneling techniques, the break-junction technique gives access to the tunneling characteristics of the interior of bulk samples; it is not restricted to a surface layer that may not be representative of the bulk material.

The sample with an overall composition of $Y_2Ba_2Cu_3O_x$ was prepared from Y_2O_3 , $BaCO_3$, and CuO powders sintered in the pressed-pellet form. The synthesis of the Y-Ba-Cu- O_x compounds is reported elsewhere. [4] The majority phase is the superconducting $Y_1Ba_2Cu_3O_{9-\delta}$ phase recently identified, [3,11,12,13] with a small addition of the semiconducting phase Y_2BaCuO_5 . The resistive (10%-90%) transition temperature is 94 K - 92 K, and $R = 0$ at 91 K. Filaments with dimensions of 1 x 1 x 20 mm were cut from a sintered 1-inch disk for preparing break junctions. The measurements were performed using a break-junction apparatus designed for dipping in liquid-helium storage dewars ($T = 4$ K). First derivatives of the I-V curves were taken using the standard lock-in technique with a modulation voltage of 1 mV.

The I-V characteristics of the $Y_1Ba_2Cu_3O_{9-\delta}$ break junctions changed as the junctions were mechanically set and reset. This is similar to the characteristics observed in the La-Sr-Cu-O system. [5,6] We think that this phenomenon was due to sample inhomogeneity, since break junction measurements on pure Pb and Sn indicate low-leakage, quasiparticle tunneling independent of junction setting. As a junction was set and reset, tunneling probably shifted between different points within the fracture, thus sampling different materials.

Figure 1 shows the predominant type of I-V characteristic and its associated dynamic conductance curve. Two traces are shown corresponding to increasing and decreasing bias voltage. This I-V curve shows little structure and is nonlinear, with a nearly quadratic dependence (nearly linear dynamic-conductance trace). This type of behavior has been observed in most of the tunneling measurements of La-Sr-Cu-O.⁵⁻¹⁰ As pointed out by Kirtley et al., [9] this is consistent with the model of Zeller and Giaever, [14] which treats tunneling in a system of small superconducting grains separated by insulating material. The nonlinearity of the I-V curve decreased at low junction resistances (less than about 100 k Ω). This curvature is not apparent at low bias in pure Pb or Sn break junctions, implying that its cause is inherent to the high- T_c compounds Y-Ba-Cu-O and La-Sr-Cu-O.

An I-V characteristic showing strong gap structure was obtained after resetting the junction several times. The data shown in figure 2 indicate low leakage tunneling between superconducting electrodes. Conductance peaks at -39 mV and +39 mV clearly define a tunneling energy gap. If the materials on either side of the junction are identical, and the junction is formed in the superconductor-insulator-superconductor (SIS) configuration, then $4\Delta/e = 78$ mV or $\Delta = 19.5$ meV. This is consistent with previous interpretations of point-contact data on the La-Sr-Cu-O system. [5-10] We have not observed a tunneling gap larger than the one reported, indicating that we are observing SIS tunneling. However, we cannot rule out that the actual junction may be in

the superconductor-insulator-normal configuration, in which case the gap would be nearly twice as large.

The peaks in the dynamic conductance (dI/dV) traces at the gap edges are broad (between 16 meV and 24 meV wide at half maximum) as shown in figure 2. Also, there is a strong negative peak in the dynamic conductance trace within 15 to 30 meV of the gap edge. If the normal state conductance varies smoothly from low bias to high bias, this represents a large negative deviation from normal-state conductance. Additional structure may exist beyond the gap edges, but was too small to be detected in these measurements.

In summary, a direct measure of the superconductive energy gap in $Y_1Ba_2Cu_3O_{9-\delta}$ gives us some information concerning the mechanism of superconductivity in this high critical-temperature superconductor. The relatively large gap of $19.5 \text{ meV} \pm 1 \text{ meV}$ gives a value of $2\Delta/k_B T_C$ of 4.8, which is consistent with the values of strongly coupled superconductors.

ACKNOWLEDGEMENTS

This work was supported at NBS by the Office of Fusion Energy, U. S. Department of Energy, Contract No. DE-AI01-84ER52113; the Office of Naval Research, Grant #N00014-86-F-0109; and by a grant from the National Engineering Laboratory, National Bureau of Standards.

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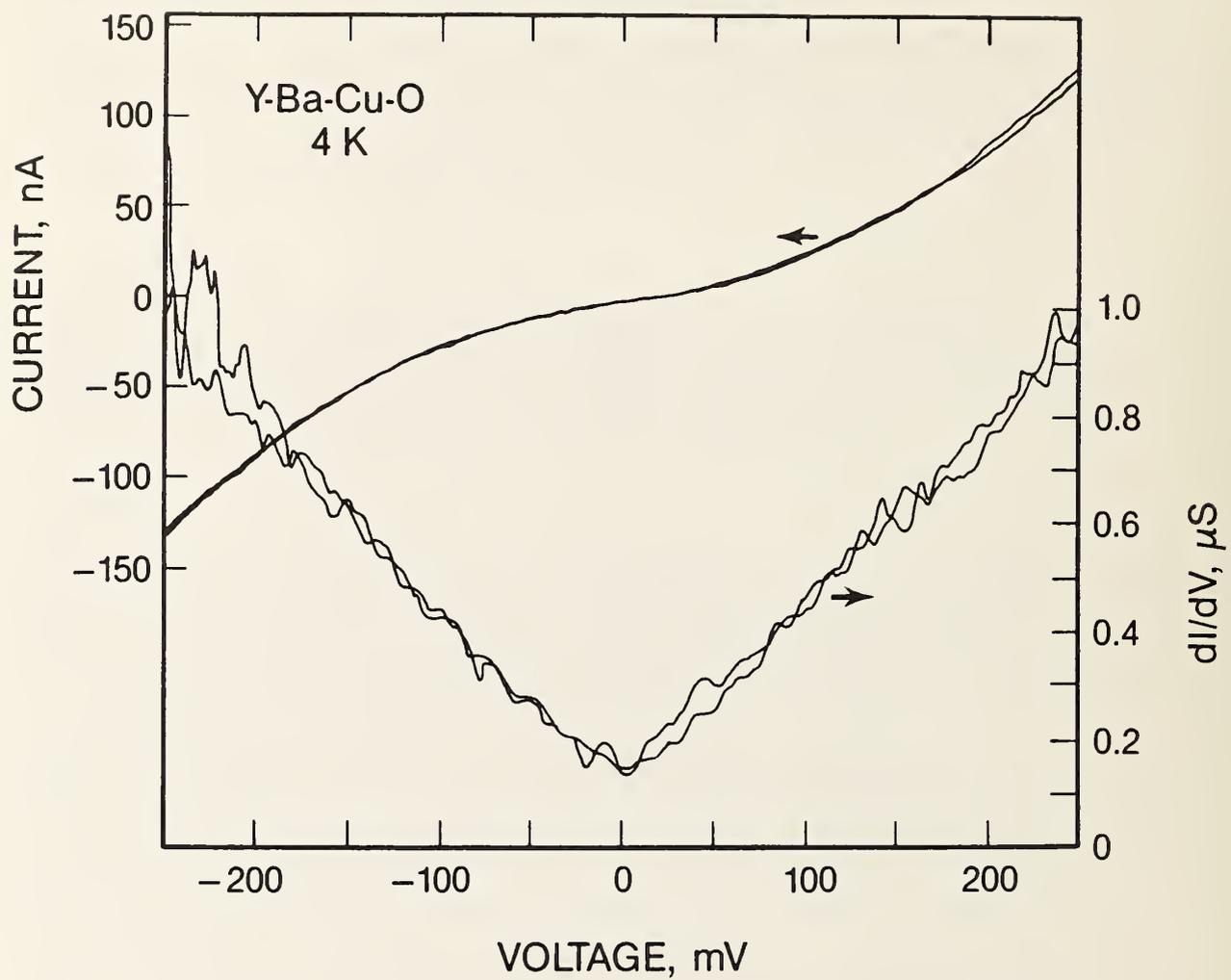


Fig. 1. Current-voltage characteristic and dynamic conductance (dI/dV) characteristic of a $Y_1Ba_2Cu_3O_{9-\delta}$ break junction immersed in liquid helium. This trace is typical of that predominately seen in the sample.

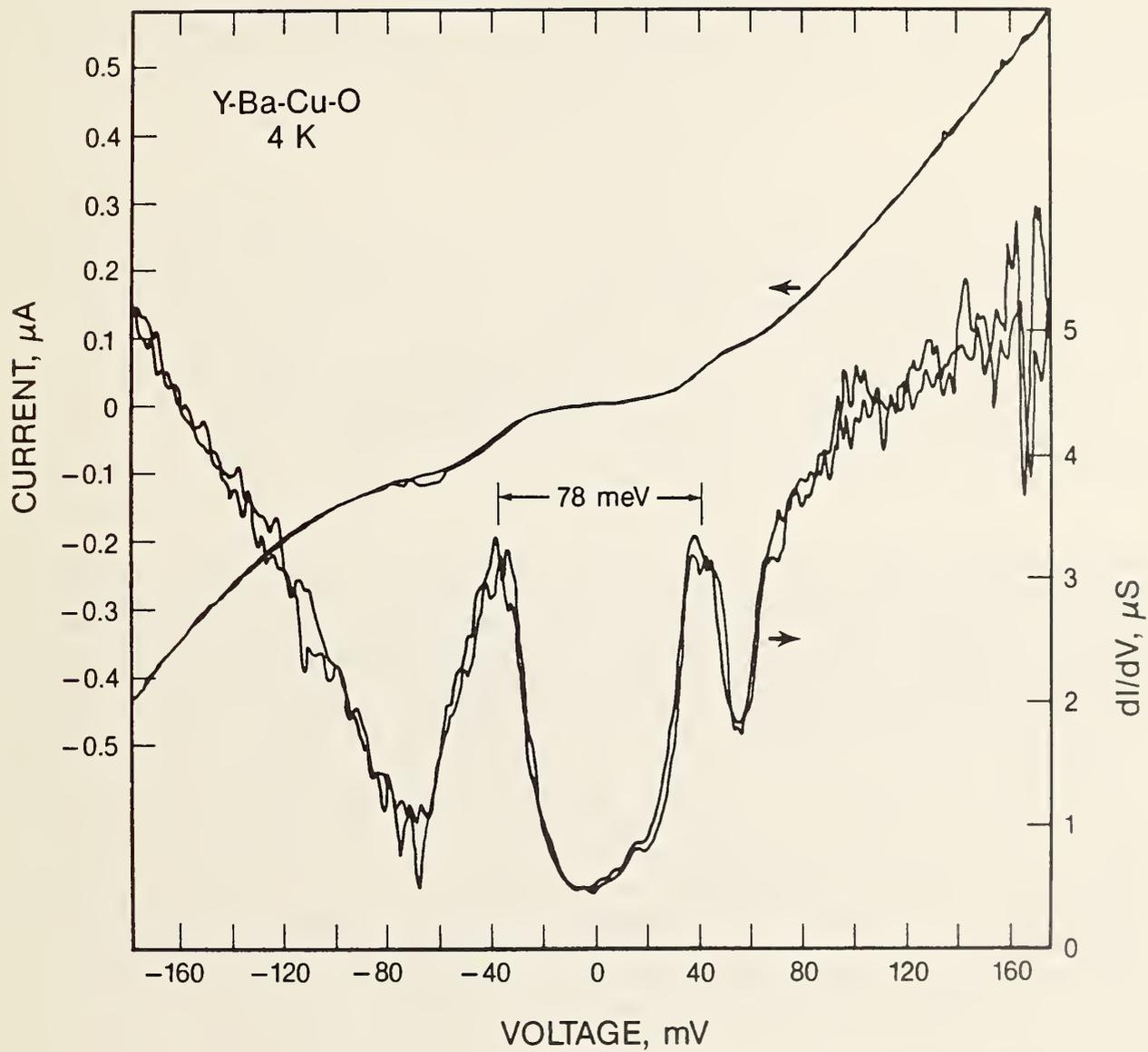


Fig. 2. Current-voltage characteristic and dynamic conductance (dI/dV) showing superconducting gap structure typical of the largest measured in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{9-\delta}$ break-junction sample.

JOSEPHSON EFFECT ABOVE 77 K IN A YBaCuO BREAK JUNCTION †

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We have observed the Josephson effect in a YBaCuO break junction. Critical currents as high as 10 mA were measured at 4 K for break junctions with a point contact within the fracture of a sample. The junction was susceptible to microwave radiation showing Shapiro steps with the ratio of V/f of $2.04 \pm 0.05 \mu\text{V}/\text{GHz}$ compared to the pair tunneling value of $h/2e = 2.068 \mu\text{V}/\text{GHz}$. These steps were clearly visible in the current-voltage characteristics at temperatures up to 85 ± 5 K.

The Josephson effect has been observed in YBaCuO by several authors. So far reported results have been point contact experiments [1-4] along with the construction of a thin film SQUID by IBM that is based on junctions formed at grain boundaries. [5] In this paper we present the first observation of the Josephson effect using break junctions. Break junctions offer the possibility of tunneling between freshly exposed surfaces of a fracture in a bulk sample.

The break junction apparatus and sample geometry is similar to that described by Moreland and Ekin. [7] A break junction is pictured in figure 1. It has a superconducting filament mounted on a bending beam. The surface strain developed by the beam is concentrated at the center of the filament so that the filament can be fractured without exceeding the elastic limit of the beam. The beam is bent using an electromagnet. Once the filament is fractured, the beam is relaxed to form a tunneling contact within the fracture of the filament. If the filament is broken in an inert environment, such as liquid helium, then the tunneling contact should be "clean."

$\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ ceramic pellets were prepared as described by Panson et al. [6] The ceramic pellets were cut to form $1 \times 1 \times 10 \text{ mm}^3$ bars, notched near their centers to facilitate the breaking process. Four terminal contacts, a voltage and a current tap on either side of the notch in the samples, were used to measure the current-voltage characteristics. Microwaves were coupled to the junction using a coaxial cable with the shield removed in the vicinity of the junction.

† Published in Appl. Phys. Lett. 51, 540 (1987).

Temperature was varied by lifting the break junction apparatus into the vapor above the liquid helium level in a storage Dewar. Temperatures were measured using a carbon resistance thermometer in the vicinity of the break junction. We estimated ± 5 K uncertainty at higher temperatures due to variable temperature gradients between the sample and the thermometer in the helium vapor.

Onset temperatures were measured on separate samples from the same batch used for the break junction measurements. The resistive onset temperature was about $97 \text{ K} \pm 0.2 \text{ K}$ with a transition width of about 3 K. The inductive onset temperature was about $90 \text{ K} \pm 0.2 \text{ K}$ with a transition width to full shielding of about 10 K. [8]

Figure 2 shows the current-voltage characteristic of the YBaCuO break junction immediately after fracturing the sample under liquid helium. Once the sample was fractured the electromagnet used to bend the break junction substrates was de-energized so that the fracture collapsed to form a point contact. Notice a well defined critical current at zero bias with an I_c of 10mA. The normal state resistance measured at a voltage of 1 mV is 0.2Ω . The $I_c R$ product is about 2 mV, well below the Bardeen-Cooper-Schrieffer theoretical prediction of $\pi\Delta/2e = 17 \text{ mV}$ [9] (assuming a BCS Δ of 18 mV^{10}). Zimmerman [11] has observed this theoretical limit in "clean" Nb point contacts formed under liquid helium. The source of the reduced $I_c R$ product in YBaCuO is unknown at this time, however, the experiment was magnetically unshielded. It is possible, therefore, that remnant fields may have caused low $I_c R$ products.

Figure 3 is a series of current-voltage curves for a YBaCuO break junction for various temperatures. In each case, 7.43 GHz microwave radiation was introduced into the helium storage dewar. Shapiro steps are visible from 4 K to 85 K as shown in the figure. The voltage step size is very close to the predicted relation for electron pair tunneling of $2eV = hf$. Theoretically, V/f should be $2.067 \mu\text{V}/\text{GHz}$ for electron pair tunneling. We observed $2.04 \pm 0.05 \text{ GHz}$ for YBaCuO. The 90 K curve illustrates the junction's susceptibility to microwave radiation, but the observed Shapiro steps are ill defined compared to those seen at lower temperatures.

With these results, we are confronted with seemingly usual and unusual point contact behavior. On one hand there is reassuring evidence for the usual pairing state associated with superconductivity. Low $I_c R$ products, on the other hand, may indicate an unusually low energy gap compared to a BCS superconductor. This may be due to a proximity contact instead of an assumed "clean" high- T_c SS contact. These assumptions, however, contradict our observation of higher gap values when the junction is in the vacuum tunneling configuration. Extremely high gap values ($\Delta = 80 \text{ meV}$) have been observed by Ng et al. [12] on samples broken at 77 K, and measured using a scanning tunneling microscope. The discrepancy between the $I_c R$ products and measured energy gaps may be due to small magnetic fields (less than one gauss) in the vicinity of the junction or there may be a self limiting field of the point contact. Alternatively, the coherence length may be short compared to the length of the microbridge in the sample fracture.

ACKNOWLEDGEMENTS

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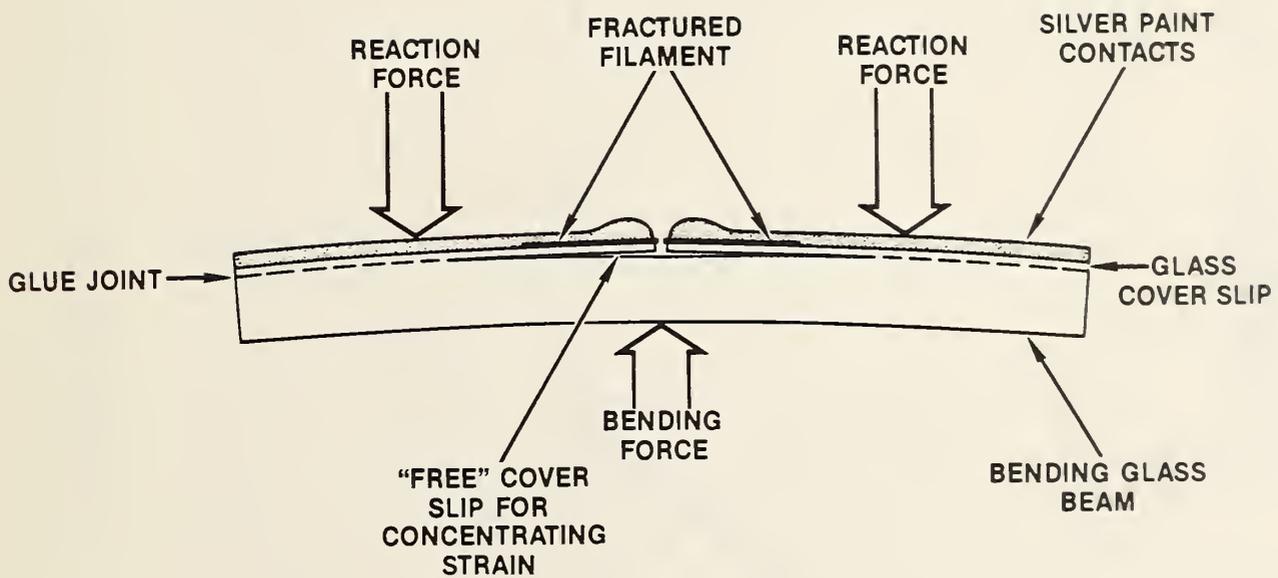


Fig 1. Break junction (after Ref. 7).

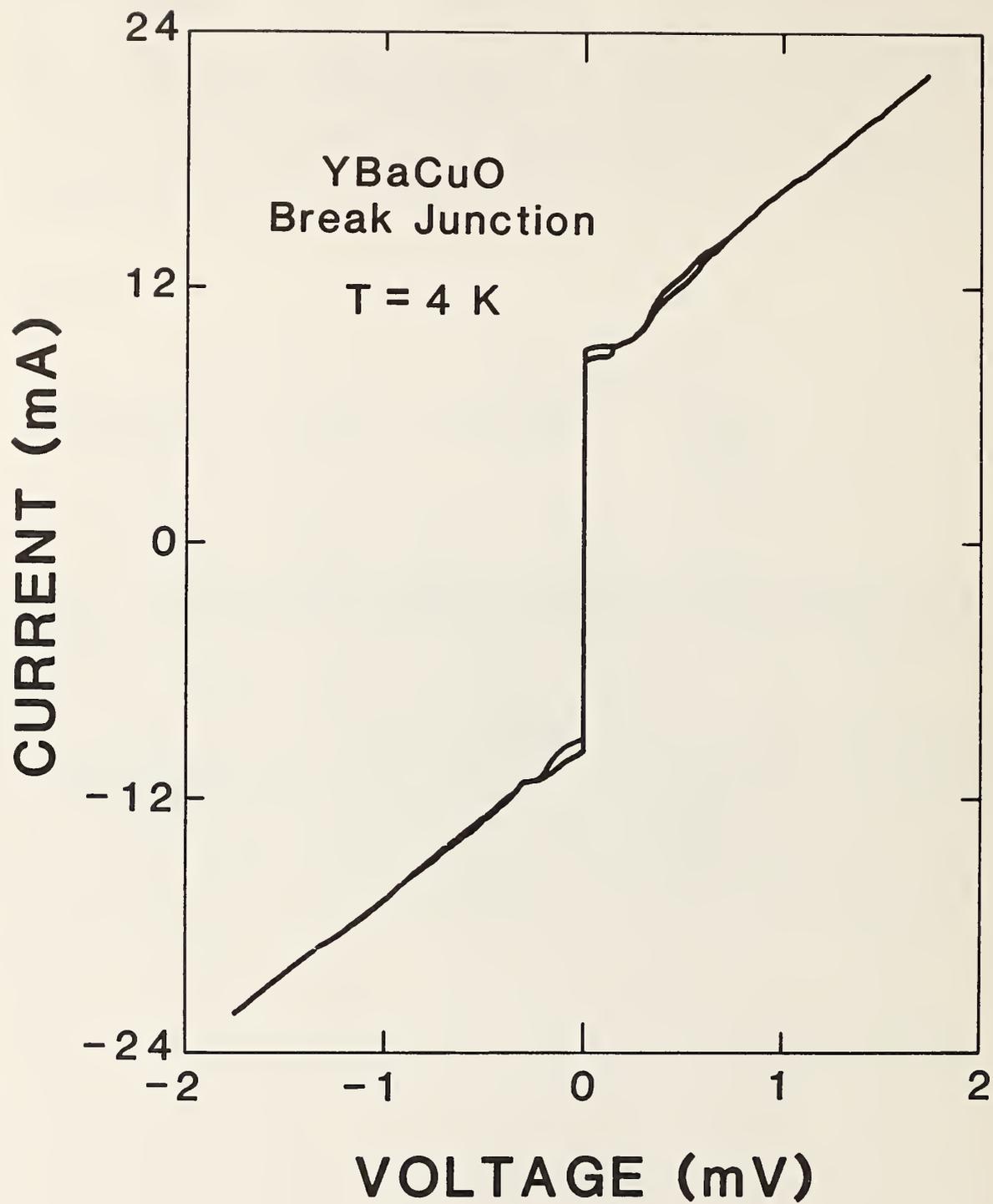


Fig 2. Point contact Josephson current in a YBaCuO break junction at 4 K. The junction was broken under liquid helium to form a clean superconducting point contact.

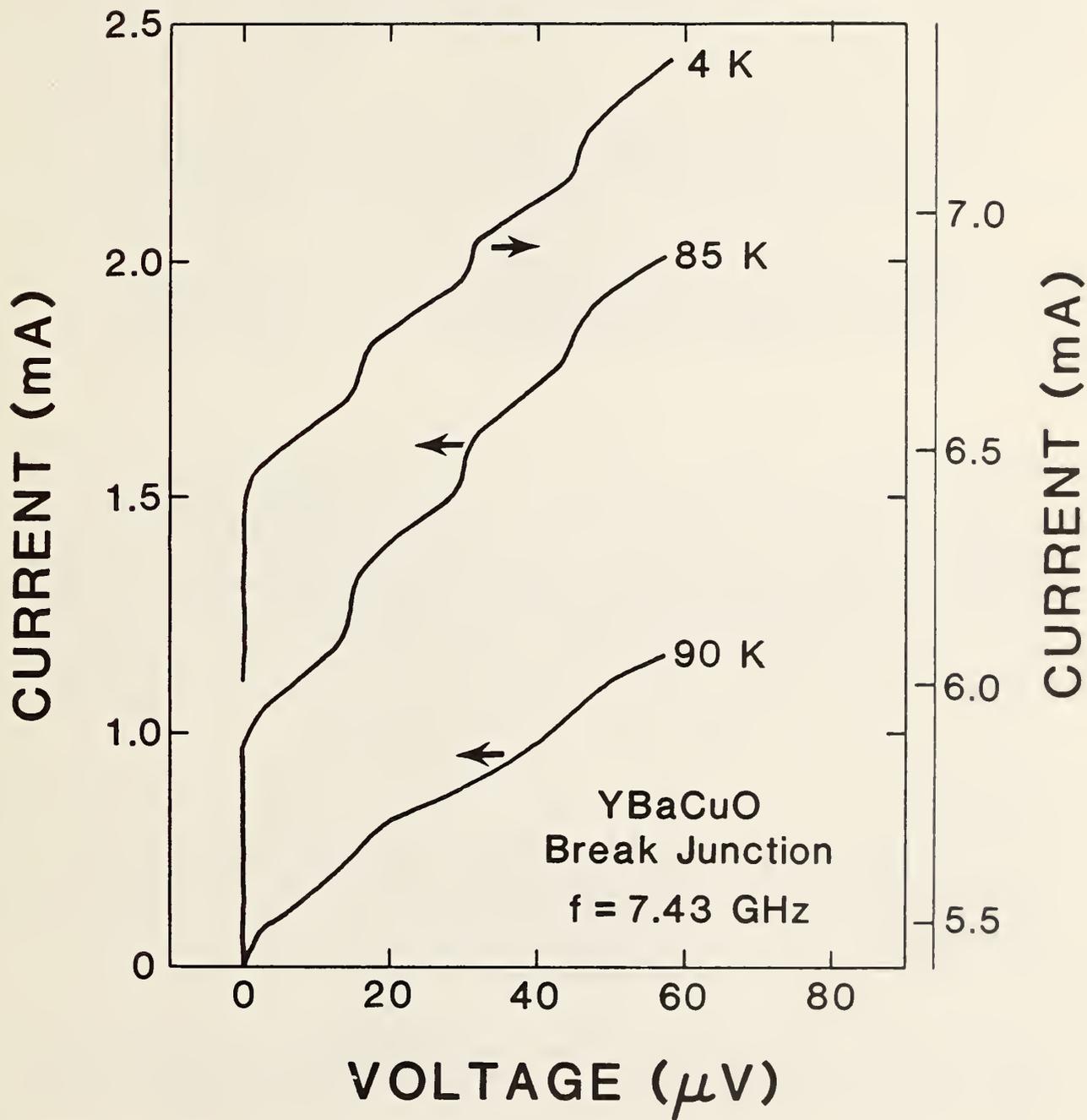


Fig 3. Shapiro steps seen in break junction current-voltage characteristics as a function of temperature. Notice that the steps are clearly visible at 85 K.

ELECTRON TUNNELING MEASUREMENTS IN LaSrCuO AND YBaCuO[†]

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The break junction technique, whereby vacuum tunneling occurs within the fracture of a bulk sample is used to study the LaSrCuO and YBaCuO perovskite superconductors. Structure in the current-versus-voltage characteristics is reminiscent of previous quasiparticle curves obtained for BCS superconducting materials. Some curves have anomalous qualities, including large dips in the junction conductance with increasing voltage just above a well defined tunneling gap edge, linearly increasing junction conductance with applied bias, features occurring near 1, 3, 5 voltage intervals.

INTRODUCTION

Previous break junction measurements [1] on Sn, Nb, NbSn, Pb, and NbTi demonstrate that this technique can be used in the same way as the more traditional oxide barrier junction technique for determining superconductive energy gaps, electron phonon couplings, and the Josephson effect. We present here break junction results for various bulk samples of the new high T_c perovskites cut from ceramic pellets. The advantages of this technique are that it can be applied to bulk materials directly, and that the freshly exposed surfaces of the fracture remain pristine if the samples are broken in an inert environment (under liquid helium for example).

EXPERIMENT

The break junction apparatus is based on an electromagnet actuator for precise control of the tunneling gap within the fracture of the samples. Experiments can be done by dipping the electromagnet-sample assembly directly into various cryogenic fluids (liquid He, Ne, or N₂) or in a variable temperature rig using He exchange gas to cool samples.

Samples were cut from ceramic pellets using a diamond wheel with ethanol cutting fluid. They were then fixed with epoxy to bendable glass substrates. LaSrCuO samples with T_c onsets of 36 K were prepared by Ku and Shelton. [2] Single phase YBaCuO samples were prepared by Kwo, Hong, and Liou, [3] and by Panson, et al. [4] with onset T_c s above 90 K.

[†] Published in High Temperature Superconductors, edited by D. U. Gubser and M. Schluter, Materials Research Society, Pittsburgh, 1987, pp. 73-75.

RESULTS

Figure 1 shows several conductance-voltage curves for LaSrCuO break junctions immersed in liquid He at 4 K. These curves are for samples taken from the same batch. Even so, the tunneling results are variable not only from sample to sample, but for different break junction settings of a single sample. Figure 1a is derived from results obtained by Moreland, et al. [5] showing classic quasiparticle behavior of a well defined tunneling voltage gap similar to that expected for strong coupled BCS superconductor with a T_c of 36 K. Figure 1b on the other hand, has a washed out gap with a linearly increasing conductance. In figure 1c the gap has disappeared. Figure 1d shows a reduced gap with strong variations (dips) in conductance as a function of voltage above the gap edge.

Figure 2 shows similar gap structures for YBaCuO break junctions immersed in liquid He at 4 K. As above, figures 2a through 2d have, respectively, a sharp gap, washed out gap, no gap, and conductance dips at higher biases. Also notice that the voltage gaps and dip locations scale roughly with T_c . Figure 2a is from reference 6.

Preliminary data taken as a function of temperature show that the gap structure disappears near T_c in both materials. However, this may not apply to the data in figures 1d and 2d since we did not vary the temperature in these instances. Also what appears to be a Josephson current has been occasionally observed in the YBaCuO break junctions. More definitive results have been obtained by Tsai, Kubo, and Tabachi. [7] They have seen Shapiro steps in YBaCuO "crack" junctions (very similar to break junctions) with the appropriate spacing of $\hbar\omega/2e$ when irradiated with microwaves.

DISCUSSION

Consider the area extent of the tunneling contact of a break junction. When the fracture is relaxed enough to measure a tunneling current the fracture surfaces do not perfectly mesh back together again. This is evident from the high junction resistances (1 k Ω to 10 k Ω) when the surfaces are shorted together. Realistic areas are, therefore, similar to those encountered using point contacts of about 1 nm [2] or less. We see that the break junction technique is a local probe extending over a few atoms of the fracture. This is consistent with the variability of the data presented above in that the perovskite structure consists of alternating layers of insulating and conducting platelets. Further, the individual conducting platelets can be superconducting or semiconducting (or both). Zeller and Giaever [8] demonstrated the effect of barrier granularity and the existence of multiple coulomb gaps on tunneling structures with results that are strikingly similar to those shown in figures 1b, 1c, 2b, and 2c.

Assuming the data in figures 1a and 2a stems from tunneling between identical BCS superconductors, we conclude that the superconductive energy gap, Δ , is 7 meV for LaSrCuO and 19 meV for YBaCuO. This gives a ratio of $2\Delta/k_B T_c$ of about 4.5 for the perovskites indicative of BCS pairing with strong electron phonon coupling. In addition, the existence of strong conductance dips at the

gap edge seen in break junction measurements of both compounds is at least consistent with the notion of strong coupling between electrons and soft phonons. This could be responsible for the high T_c s of these perovskites as discussed by Weber. [9] Alternatively, the conductance dips could be remnants of a 1, 3, 5, ... series of voltage steps caused by multiple particle tunneling [10] or a single coulomb gap [11] intrinsic to each material.

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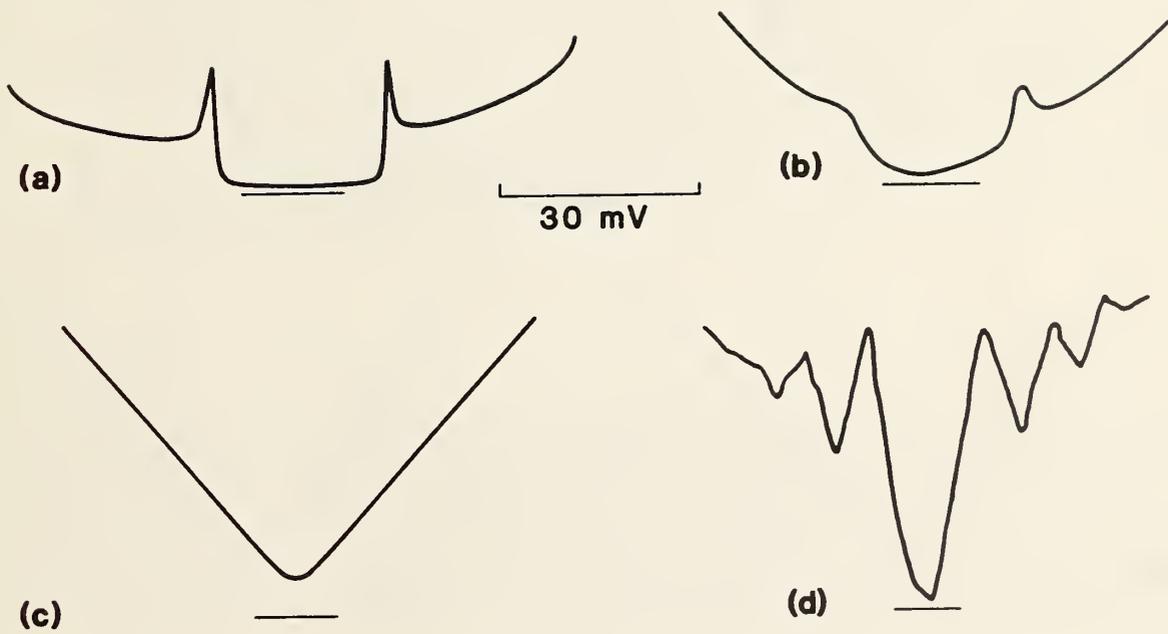


Fig. 1. Conductance vs. voltage curves for LaSrCuO break junctions in liquid He at 4 K.

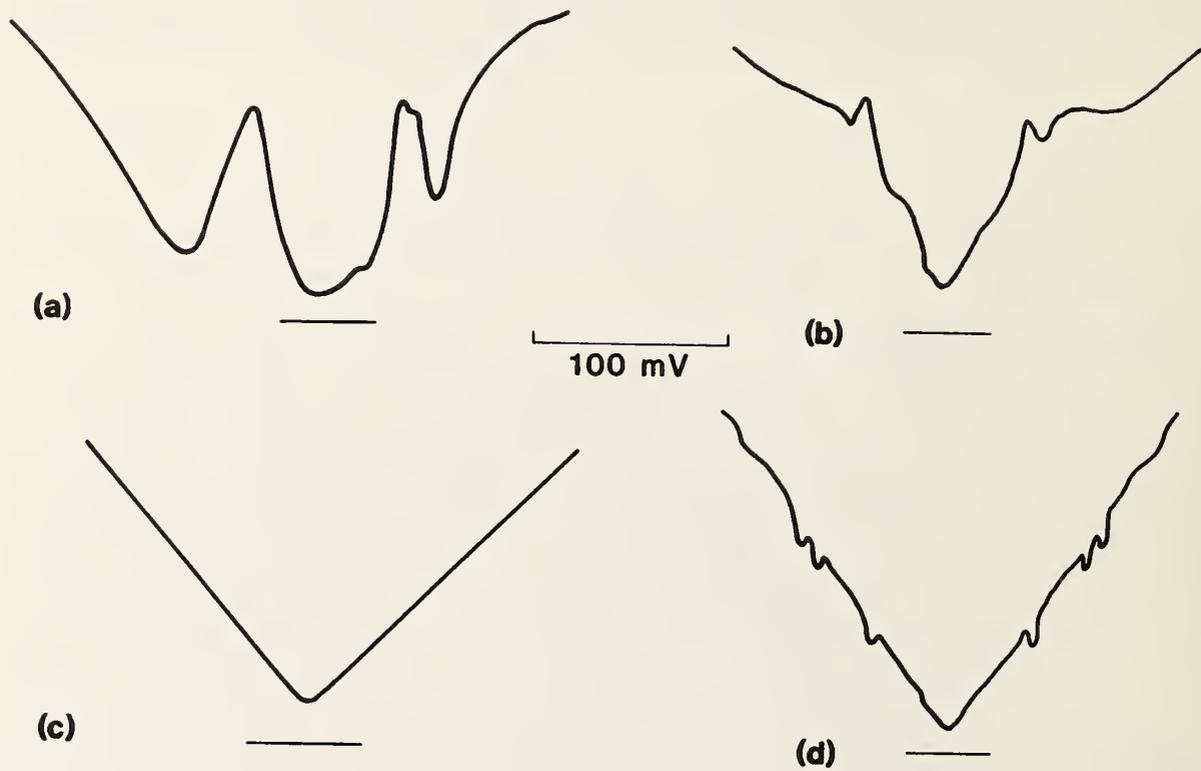


Fig. 2. Conductance vs. voltage curves for YBaCuO break junctions in liquid He at 4 K.

ELECTRON TUNNELING MEASUREMENTS OF HIGH T_c COMPOUNDS USING BREAK JUNCTIONS†

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We report on the break junction technique and its application to the high T_c superconductors LaSrCuO and YBaCuO. In this technique, bulk samples are fractured and the freshly fractured surfaces adjusted to form a tunneling junction with vacuum or liquid helium as the insulating barrier. Precise mechanical adjustment permits the study of electron tunneling phenomena between pieces of a bulk superconductor. The current voltage characteristics of these break junctions are variable indicating sample inhomogeneity. However, some junction settings result in the more familiar quasiparticle signatures in the current voltage characteristics. Low leakage junctions indicate the presence of a sharp superconductive energy gap as well as large variations in junction conductance above the gap edge in both materials.

INTRODUCTION

The break junction technique [1] has been used to investigate the electron tunneling properties of the newly discovered high T_c superconductors. [2-5] We present here a summary of break junction measurements on LaSrCuO and YBaCuO. Though some aspects of these tunneling results appear to have the usual behavior when compared to BCS theory, anomalous characteristics are usually observed in these materials. Such characteristics may stem from the granular nature of the samples tested and weak-link coupling between grains.

EXPERIMENT

Break Junction Apparatus

A break junction is pictured in Fig. 1. It has a superconducting filament mounted on a bending beam. The surface strain developed by the beam is concentrated at the center of the filament so that the filament can be fractured without exceeding the elastic limit of the beam. The beam is bent using an electromagnet. Once the filament is fractured, the beam is relaxed to form a tunneling contact within the fracture of the filament. If the

† Published in Jap. J. Appl. Phys. 26, Supplement 26-3, 999 (1987).

filament is broken in an inert environment, such as liquid helium, then the tunneling contact should be "clean."

Samples

$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ceramic pellets were prepared by Ku and Shelton at Ames-Iowa State University [6]. The T_C of this material was 35 to 36 K. $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ ceramic pellets were prepared by Hong and Kwo [7] at AT&T, and Panson, et al. [8] at Westinghouse. The T_C of these materials was 93 K.

RESULTS

Vacuum Tunneling in LaSrCuO

A summary of the types of LaSrCuO break junction results is shown in figure 2. A variety of behavior can be seen as the junctions are set and reset (opened and closed). Figure 2a is indicative of SIS quasiparticle tunneling. The energy gap, Δ , determined from the location of the peaks in the conductance-voltage curves is 7 meV. This is consistent with a strong coupling BCS theory in that $2\Delta/k_B T_C$ is about 4.5. Figure 2b shows washed out yet still discernable gap structure. The most commonly observed characteristic is shown in figure 2c. Linearly increasing junction conductance has been observed in granular tunneling junctions by Zeller and Giaever [9] and attributed to the existence of a distribution of Coulomb voltage gaps.

Large variations in the conductance above the gap edge are sometimes observed in LaSrCuO break junctions as shown in figure 2d. This structure in the current-voltage characteristic may be due to the electron coupling mechanism. Alternatively the structure may stem from multiparticle tunneling or the existence of a single Coulomb voltage gap as observed by Barner and Ruggerio [10].

Vacuum Tunneling in YBaCuO

We have observed results for YBaCuO break junctions (see Fig. 3) that are similar to those for LaSrCuO break junctions. The energy gap scales with T_C . The ratio $2\Delta/k_B T_C = 4.8$ at $T = 4$ K (the measured Δ was 19.5 meV).

Point Contact Tunneling in LaSrCuO

The fracture in a break junction sample can be adjusted to form a point contact. Thus far, we have observed only hints of Josephson supercurrents in LaSrCuO break junctions. A few junctions had small conductance peaks at zero bias.

Point Contact Tunneling in YBaCuO

Superconducting point contacts have been observed with the break junction technique in YBaCuO. Figure 4 shows a current-voltage characteristic for a YBaCuO break junction irradiated with microwaves ($f = 7.43$ GHz) at $T = 85$ K.

The spacing of the Shapiro steps is $2.04 \pm 0.05 \mu\text{V}/\text{GHz}$, close to the appropriate value of $h/2e = 2.068 \mu\text{V}/\text{GHz}$ for pair tunneling.

At higher biases we observed switching phenomena in the current-voltage characteristics. Figure 5 shows such a characteristic for various temperatures below T_c . Notice the Josephson supercurrent, barely visible at zero bias, with an I_c of about $500 \mu\text{A}$ at 4 K. Switching occurs with increasing voltage (at higher voltages while increasing voltage and at lower voltages while decreasing voltage). As temperature increases from 4 K towards T_c , the switching features in the junction characteristics move in from higher biases and the hysteresis decrease, disappearing all together at T_c . This behavior is typical of heating effects in microbridges as sections of the microbridge become normal with increasing current flow.

CONCLUSION

There is evidence for of an intrinsic energy gap that can be detected using tunneling spectroscopy in the high T_c compounds LaSrCuO and YBaCuO . The energy gap scales with T_c of the material. The energy gap decreases and vanishes when approaching T_c from lower temperatures. We believe, therefore, that the tunneling energy gap is quasiparticle in nature and not Coulombic.

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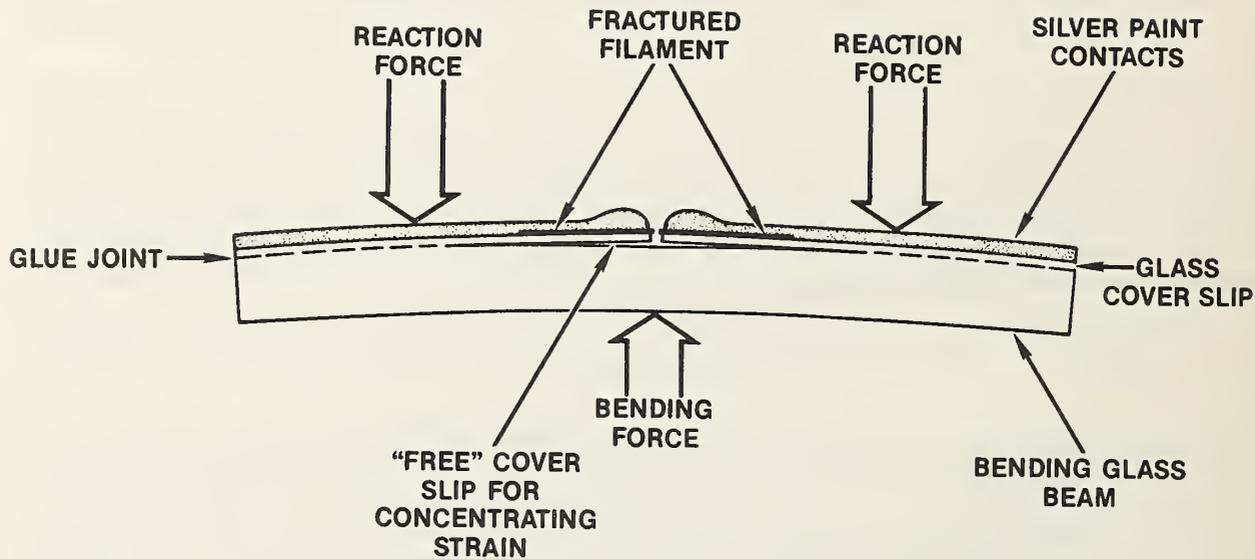


Fig. 1. Break junction (after ref. 1).

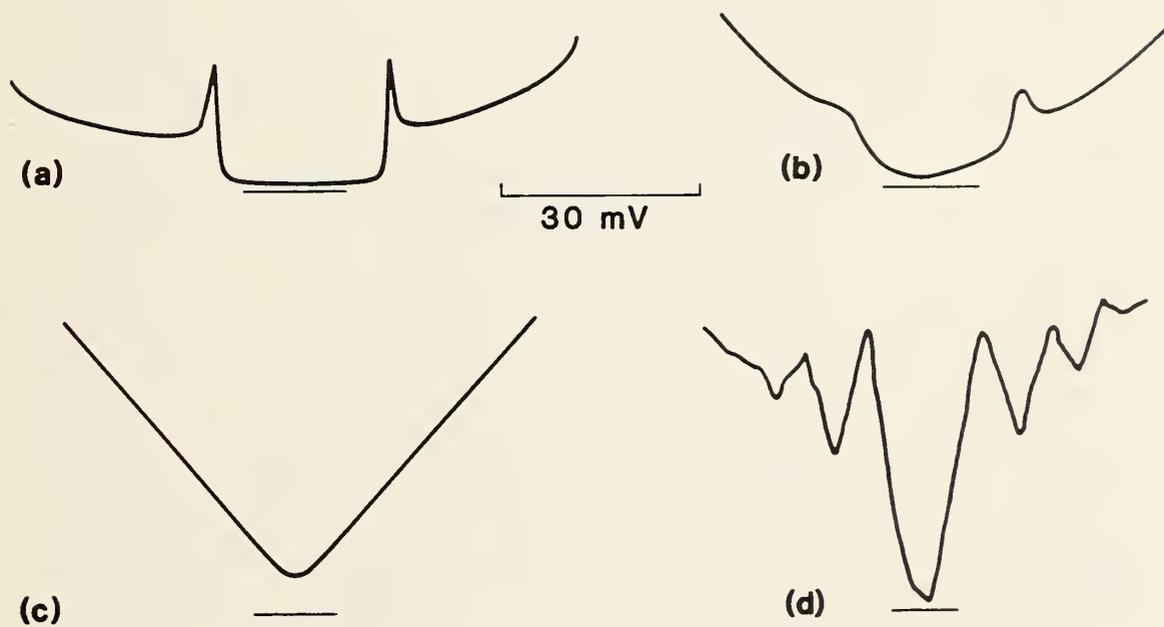


Fig. 2. Conductance-voltage curves for LaSrCuO break junctions in liquid helium at 4 K (after ref. 5).

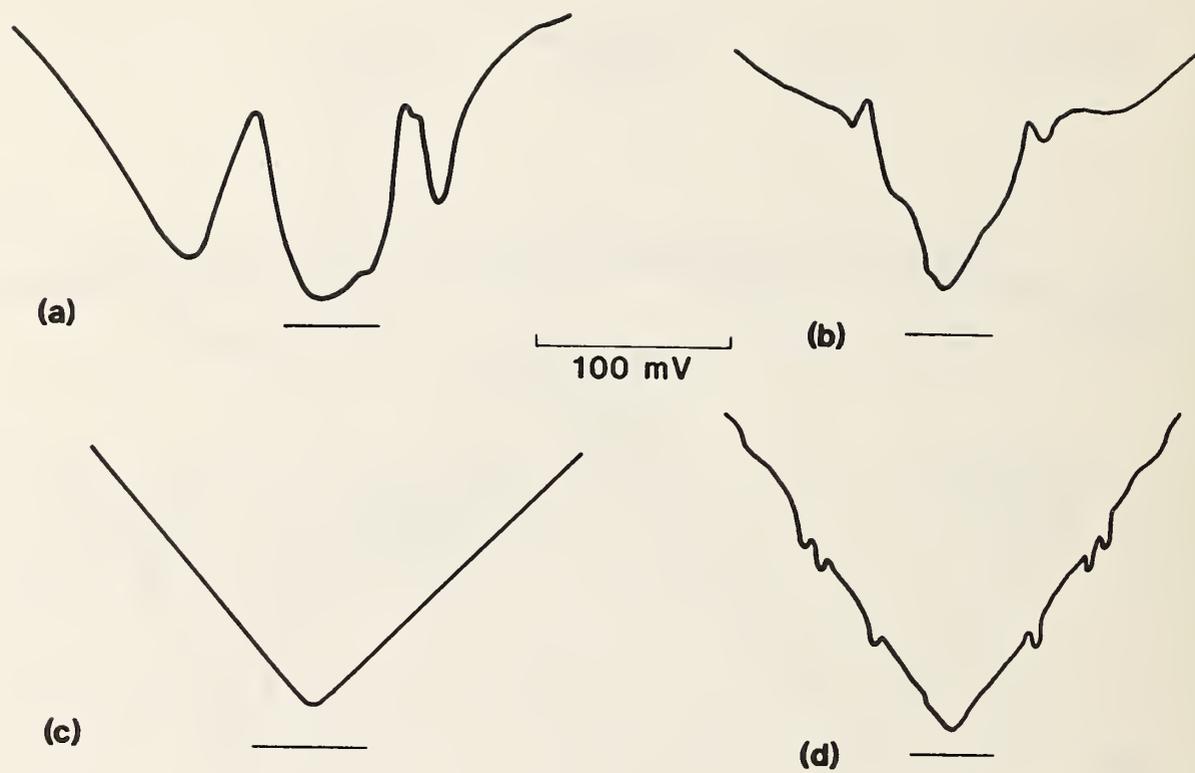


Fig. 3. Conductance-voltage curves for YBaCuO break junctions in liquid helium at 4 K (after ref. 5).

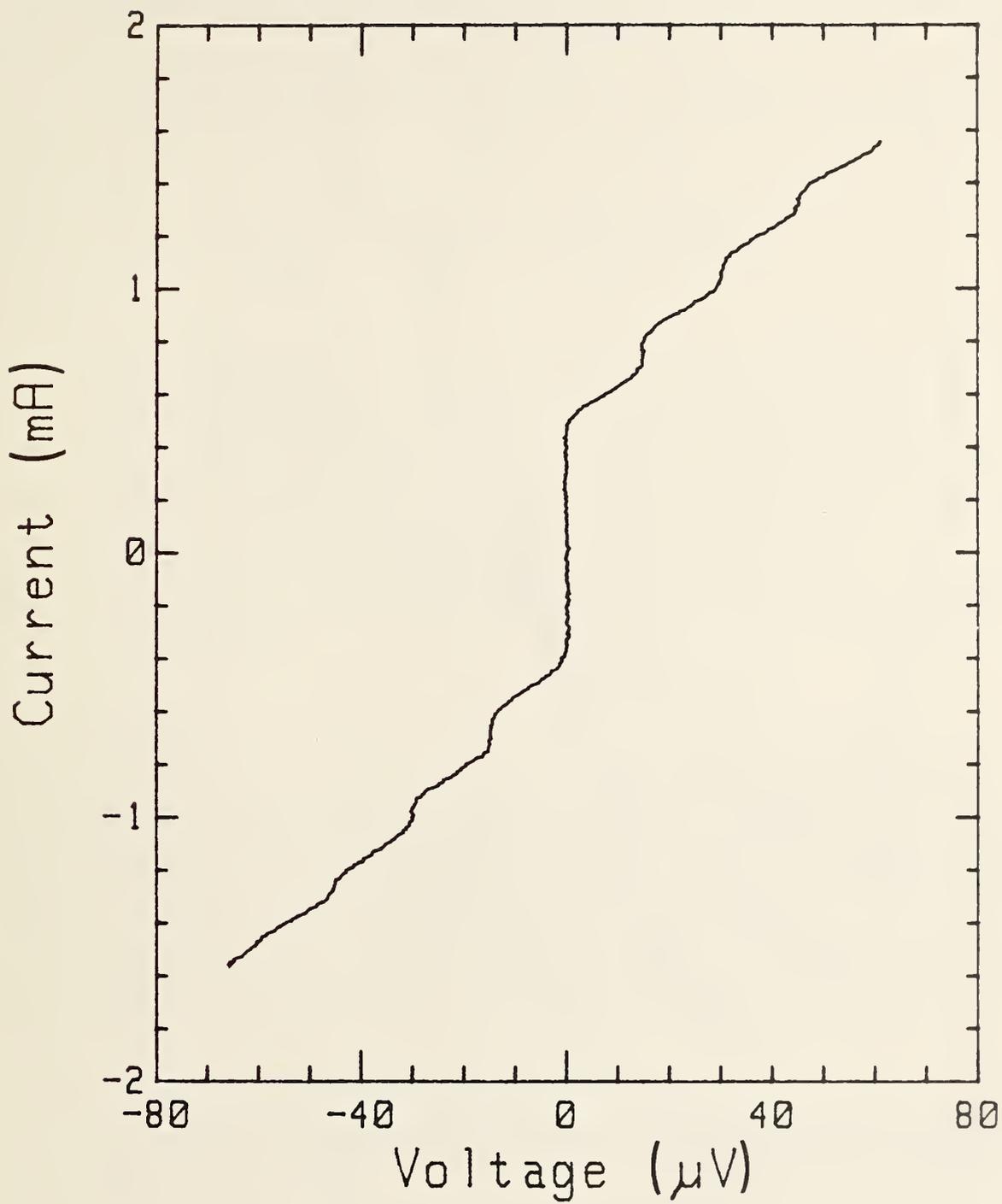


Fig. 4. Current-voltage curve for a BaCuO break-junction point contact showing a Josephson current at 85 K ($f = 7.43$ GHz).

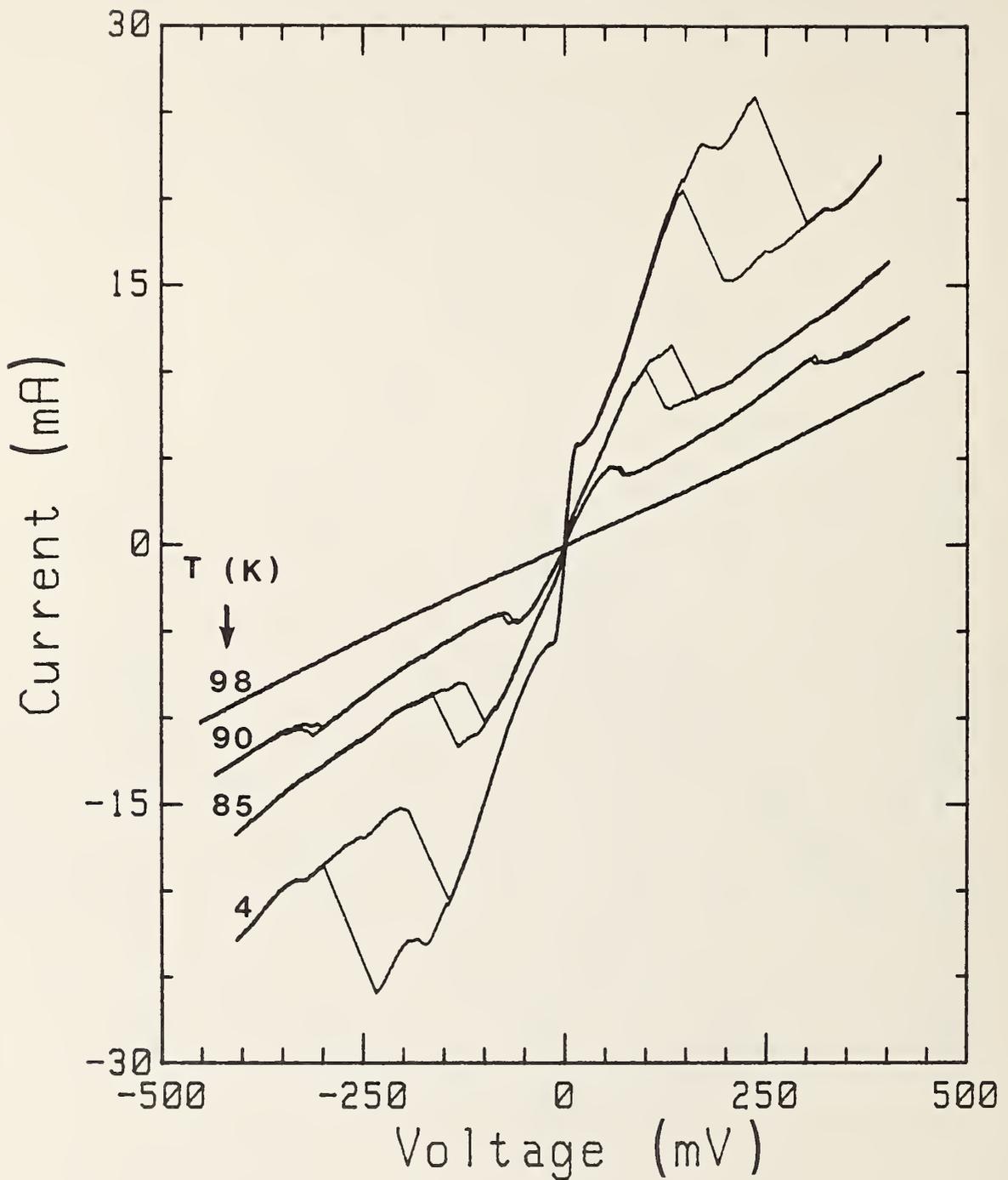


Fig. 5. Current-voltage curves for a YBaCuO break-junction point contact at various temperatures.

ANOMALOUS BEHAVIOR OF TUNNELING CONTACTS IN SUPERCONDUCTING PEROVSKITE STRUCTURES†

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Our break junction results for electron tunneling spectroscopy of the perovskite superconductors La-Sr-Cu-O and Y-Ba-Cu-O are similar to those obtained using thin film, scanning tunneling microscopy, and point contact methods. Energy gap structures are sometimes observed in the measured current voltage characteristics. More often, however, the characteristics are anomalous when compared to previous tunneling studies of BCS superconductors. The anomalies include linearly increasing conductance with voltage, large deviations in junction conductance above the gap edge, and junction diode action. We discuss some possible explanations for these observations.

INTRODUCTION

Several techniques have been used for electron tunneling spectroscopy of the perovskite superconductors La-Sr-Cu-O (LSCO) and Y-Ba-Cu-O (YBCO) (see Table 1). The purpose of this paper is to compare and contrast our results obtained using the break junction technique to similar results obtained using thin films, scanning tunneling microscopes, and point contacts. In general, current-voltage characteristics show energy gap spectra with detailed structure at high junction biases but the data are variable even for a given technique on a given sample. In addition, current-voltage curves are generally nonlinear and show rectification.

Some of this tunneling behavior may be microstructural in origin and not related to the electron coupling mechanism (phonons, plasmons, excitons, ...). We discuss three types of model microstructures that may exist in the vicinity of the tunneling contact and their possible effects on tunneling current-voltage characteristics. The first model is based on the experiments done by Zeller and Giaever [1] on granular tunneling structures. This model is adapted by Kirtley et al. [2] to perovskite superconductors. The second model is based on a series of superconducting tunnel junctions within the vicinity of the tunneling contact in the perovskite material as proposed by Kapitunik.

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[3] Finally, we propose a third model based on the laminar nature of a single crystal grain of a perovskite material. In this model individual laminae form a series-parallel network of superconducting junctions within a single grain of the material.

EXPERIMENT

A break junction is described in ref. 4. It has a superconducting filament mounted on a bending beam. The surface strain developed by the beam is concentrated at the center of the filament so that the filament can be broken without exceeding the elastic limit of the beam. The beam is bent using an electromagnet. Once the filament is fractured the beam is relaxed to form a tunneling contact within the fracture of the filament. This contact may be a through a thin insulating medium (vacuum, gas, or liquid) or the fracture can be closed to form a point contact. Precise control of the tunneling gap approaching picometer sensitivity is afforded by the electromagnet bending assembly.

Experiments can be done by dipping the electromagnet-sample assembly directly into various cryogenic fluids such as liquid helium, neon, or nitrogen or in a variable temperature rig using helium exchange gas to cool the samples. If the filament is broken in an inert environment such as liquid helium then the tunneling contact is probably clean.

Samples were cut from calcined ceramic pellets using a diamond wheel and ethanol cutting fluid. They were then fixed with epoxy to glass break junction substrates. $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ samples with T_c onsets of 36 K were prepared by Ku and Shelton. Single phase $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ were prepared by Kwo, Hong and Liou and by Panson et al. with onset T_c 's above 90 K. Four terminal contact to the samples was done using silver paint. The silver paint-sample contact resistance was between 1 and 10 Ω .

RESULTS

A summary of the tunneling results known to us at this time is shown in Table 1. Detailed experimental data can be found in the cited references. This summary describes both qualitative features of the curves as well as characteristic voltages where structures in the tunneling spectrum occur. The tunneling experiments fall into three categories - break junctions, STM and point contact, and thin film junctions. The STM and point contact methods are similar in that the STM is used in a stationary mode and generally the STM tip is touching the surface of the sample. A central observation in these experiments is that the tunneling results show variability even for measurements of different points on the same sample. Linearly increasing conductance as a function of voltage is commonly observed. In addition, a staircase pattern where the conductance increases in steps with increasing bias has been reported along with other large variations in conductance with increasing bias. These features in the conductance voltage curves may be occurring near harmonics of the fundamental gap voltage. Finally, the curves are asymmetric to varying degrees about zero bias. This may be due to a semiconducting

sample surface that forms a Schottky barrier or to an asymmetric tunneling barrier.

Junction leakage is the ratio of the junction conductance at zero bias to junction conductance just above any observed gap edge in the tunneling spectrum. In most cases the leakage is high compared to that for oxide barrier junctions of Pb, for example, where leakages on the order of 0.01 are possible. This may not be surprising since tunneling may be occurring through a Schottky contact or narrow-band semiconductor on or within the material. Also, point contact and STM experiments may have high junction leakage because the counter electrode tip is pressed into the sample.

The electrode configuration is the inferred type of tunneling junction, i.e. SS for superconductor-superconductor tunneling, SN for superconductor-normal metal tunneling or SS' for superconductor-superconductor tunneling between different superconductors. The actual configuration is somewhat uncertain since the Josephson effect has been observed in point-contact experiments where the point is made of a normal metal, indicating that the junction is actually inside the superconducting sample and not at the sample surface. This possibility may apply to all measurements and though the SN configuration seems appropriate, there may be SS tunneling instead.

The ratio $2\Delta/k_B T_c$ should be equal to 3.5 for a BCS superconductor in the weak coupling limit. Strong coupling BCS superconductors have ratios as high as 5.0. Here, Δ is the superconductive energy gap as measured from the location of the conductance peaks in the tunneling spectrum. These peaks are presumably caused by peaks in the quasiparticle density of states. For SN tunneling the first peak occurs at Δ/e . For SS tunneling the first peak occurs at $2\Delta/e$. Note that the ratios for SN tunneling may be half the reported values because, as discussed above, the junction may be in the SS configuration. A spectral pattern or sequence of peaks in the conductance-voltage curve sometimes occurs at voltages near multiples of the energy gap. This phenomenon is generally observed in oriented films where the tunneling direction is perpendicular to the c axis of the layered structure. It has also been observed in bulk samples where there may not be any grain orientation. Such harmonic structure may be microstructural in origin or may be due to the coupling mechanism for electron pairing.

Some of the tunneling curves show a Josephson supercurrent at zero junction bias. The type of Josephson effect is indicated in table 1. ac and dc Josephson effects have been seen and SQUIDs have been made from YBCO films and point contacts.

Table 1. Summary of electron tunneling experiments on LSCO and YBCO

Description	Junction leakage	Electrode configuration	$2\Delta/k_B T_C$	Spectral pattern	Josephson effect	Ref.
LSCO break junction	0.05	SS	4.5	**	**	9
LSCO break junction	0.05	SN	4.5	1,3,5	**	10
Pt-Rh to LSCO STM	0.05	SN	3.5-6.3	1,3,5	**	2
Pt-Rh to LSCO STM	0.50	SN	5-9	**	**	11
Au to LSCO point contact	0.10	SN	8-14	**	**	12
W to LSCO thin-film STM	< 0.001	SN	8-18	1,3,5	**	13
Pb thin-film to LSCO thin film	0.10	SS'	8-18	**	**	13
Al to LSCO point contact	0.80	SN	4-5	**	**	14
Cu to LSCO point contact	1.0	SN	4.5	1,2,3	**	15
Al to LSCO point contact	**	SN	**	**	ac, dc	16
YBCO break junction	0.10	SS	4.8	**	**	17
YBCO break junction	0.20	SN	4.7	1,3,5	**	18
Pt-Ir to YBCO STM	0.30	SN	4.3	**	**	19
Pb thin film to YBCO	**	SN	10.5	1,2,3	**	20
W to YBCO point contact	< 0.001	SN	13	1,3,5	**	21

Table 1. Summary of electron tunneling experiments on LSCO and YBCO (cont.)

Description	Junction leakage	Electrode configuration	$2\Delta/k_B T_C$	Spectral pattern	Josephson effect	ref.
Pt-Rh to YBCO STM	0.20	SN	20	**	**	22
Nb to YBCO point contact	**	SS'	**	**	ac	23
YBCO crack junction	**	SS	**	**	ac, dc	24
YBCO break junction	**	SS	**	**	ac	25
NbZr to YBCO point contact	**	SS'	**	**	ac	26
YBCO to YBCO point contact	**	SS	**	**	ac	26
YBCO thin-film to YBCO thin-film	**	SS	**	**	dc SQUID	27
YBCO to YBCO point contact	**	SS	**	**	ac SQUID	28

** not reported

DISCUSSION

It is difficult at this time to decide what are good data or which technique is the most viable for electron tunneling spectroscopy of the superconductive energy gap in the perovskite superconductors. The biggest problem probably stems from the inhomogeneity in these samples and/or the transport anisotropy of the individual crystals in a polycrystalline matrix. Most if not all of the tunneling techniques probe small areas of the sample and may be sensitive to material variations approaching atomic scales. Some caution should be taken, therefore, when interpreting the results. The local T_C may not be the bulk value determined resistively or inductively. Also, T_C may be pressure dependent. Pressure within the samples induced by the point contact may result in an anomalously high Δ especially if the load is distributed over a small contact area. Presumably for high resistance break junctions ($R > 1 \text{ M}\Omega$) and film contacts this is not a problem since the induced pressure should be

smaller. The break junction technique has the additional appeal of probing freshly exposed surfaces within a fractured material.

Large features in the conductance-voltage curves occurring near the given voltage sequences may be related to fundamental modes that participate in the electron pairing mechanism. For example, Weber has calculated the phonon density of states and electron coupling parameters for LSCO.²⁹ He finds that low energy (soft) phonons could be responsible for the high T_c in LSCO of 36 K. Though this calculation is pushing the limits of the Eliashberg formalism, there is evidence for the existence of these soft modes in the tunneling data. As T_c 's become larger and larger, however, the soft phonon theory becomes less appealing. Further, there is the possibility that the microstructure near the tunneling contact may be causing the features in the conductance-voltage curves. The three following models, or combinations thereof, may account for the data.

Granular Model

In the granular model the superconductor is actually divided into superconducting grains isolated from each other by insulating tunneling barriers. This model was first proposed by Zeller and Giaever¹ for granular Sn junctions. They observed a linearly increasing conductance with voltage and attributed this to the existence of a distribution of coulombic energy gaps due to the capacitance of individual grains. The grain size must be about 20 nm or less in order to cause such a zero bias anomaly. If the particles are identical, or their size distribution is peaked, i.e. if there is a single coulomb gap associated with charging the isolated grains, then the conductance-voltage curves may show a staircase pattern in the 1,3,5 sequence. This effect has been seen by Barner and Ruggiero in granular Ag tunnel junctions. [30]

The 1 μm grain size typical of the perovskite superconductors seems much too large to cause these tunneling spectrum features. A linearly increasing conductance curve may therefore indicate intergranular inhomogeneity. Further, peaks in the conductance-voltage curve occurring at a 1, 3, 5,... sequence may indicate an intrinsic regular inhomogeneity.

Multiparticle Model

This model, proposed by Kapultulnik, [3] assumes that the grains are oriented to form a series array of junctions near a primary tunneling contact. If this series is in a NSSS... configuration then one might expect that the conductance peaks would occur at a 1, 3, 5,... voltage sequence. If the series is SSSS... then peaks might occur at a 2, 4, 6,... voltage sequence. However, for a series array of junctions with similar resistances one would expect the array to switch to the normal conducting state at a voltage corresponding to the sum of the gaps resulting in an apparently large tunneling energy gap and not in a staircase 1, 3, 5,... pattern.

Laminar Model

We propose another model that leads to conductance steps in a 2, 6, 10, ... sequence, thus reconciling some of the tunneling measurements of Δ . Essentially the proposed microstructure would consist of a complex tunneling matrix with parallel superconducting laminae connected to each other, the point contact, and the surrounding grains by tunneling junctions. This structure may be manifested within a single crystal grain, for example as a layered perovskite, with superconducting layers separated by high dielectric insulating barriers.

Let R_{11} be the resistance between adjacent laminae within a grain. Let R_{g1} be the resistance between the surrounding grains and a single lamina, and let R_{p1} be the resistance between the point contact and several laminae of the grain. These laminae form the primary junction of the contact. Further let us assume that R_{11} is much larger than R_{g1} and R_{p1} . Under these conditions we expect steps in the conductance to occur at a 2, 6, 10, ... sequence. The first step occurs at $2\Delta/e$ because the primary junction has the NISIN configuration. By adjusting the point contact it should be possible to make the primary junction nearly symmetric, that is, R_{p1}^D is roughly equal to R_{p1}^P . This means that the primary laminae are at a voltage close to half the applied bias. When they reach a voltage of $3\Delta/e$ (V bias = $6\Delta/e$) then tunneling can also occur through an adjacent laminae following a SISIN series. The key point is that the voltage drop across peripheral adjacent laminae can not exceed $2\Delta/e$ if R_{g1} is much larger than R_{11} so the next adjacent layer begins to contribute to the conductance of the contact when the first adjacent layer reaches $3\Delta/e$ (primary laminae at $5\Delta/e$, V bias at $10\Delta/e$) and so on.

CONCLUSION

Which of these models (if any) apply to the perovskite superconductors? The gap features of the tunneling spectra generally disappear upon warming through T_c , whereas the zero bias anomaly persists, though thermally smeared with increasing temperature. Also, the energy gap scales with the T_c s of the two compounds. These facts indicate that the staircase pattern in the conductance-voltage curves is probably not caused by sample microstructure as in the granular model, but that granularity exists nonetheless. Perhaps the important energy gap measurement is not that of the largest tunneling gap but that of the tunneling gap that is the common denominator of all tunneling measurements.

ACKNOWLEDGEMENTS

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by

John Moreland, J. W. Ekin, and A. F. Clark

METHOD AND APPARATUS FOR FORMING
MECHANICALLY ADJUSTABLE BREAK JUNCTIONS
FOR ESTABLISHING AN ELECTRON TUNNELING CURRENT

BACKGROUND OF THE INVENTION

This invention relates generally to electron tunneling junctions and in particular to mechanically adjustable break junctions for establishing an electron tunneling current across a fracture in a conducting material.

With the advent of quantum mechanics, Frenkel realized that electrical conduction due to the overlap of the electron clouds surrounding two electrodes could be detected if they were separated by a distance of less than about two nanometers. See, for example, J. Frenkel, Phys. Rev., 36, 1604 (1930). Later, in the early sixties, Giaever found that a native oxide tunneling barrier satisfied this requirement and was stable enough for electron tunneling spectroscopy experiments. See, I. Giaever, Rev. Mod. Phy., 46, 245 (1974). Such measurements indicated that the oxide barrier was mechanically stable to within a small fraction of an atomic diameter (less than a picometer). Recently the oxide barrier concept has been extended to materials that grow inadequate native oxides with the development of

artificial tunneling barriers consisting of deposited layers of oxidized metals. See, for example, D. A. Rudman and M. R. Beasley, *Appl. Phys. Lett.* 36, 1010 (1980).

The scanning electron tunneling microscope (STM) invented by Binnig and Rohrer has sparked new interest in mechanically controlling tunnel barriers. See, G. Binnig, H. Rohrer, C. Gerber and E. Weibel, *Appl. Phys. Lett.* 40, 178 (1982). Mechanically controlling relative displacements of two electrodes for meaningful tunneling measurements can be a difficult task. Thermal as well as electromechanical drifts can cause unwanted apparatus deformations. However, experimentalists have been driven by the prospect of tunneling into new materials that form inadequate oxides by replacing oxide barriers with a vacuum, gas or liquid gap. Though the STM has been used mainly to study surface topography, it has recently been adapted for tunneling spectroscopy.

Squeezeable electron tunneling (SET) junctions developed by Hansma, Moreland and Alexander (Patent No. 4,566,023 incorporated by reference) have also been used to establish ultrastable mechanically adjustable tunneling barriers. This is facilitated by the compact SET junction construction. In other words, the transverse scanning mobility of the STM was sacrificed for increased SET junction stability necessary for higher resolution tunneling spectroscopy.

In the initial work on piezo-electric systems for mechanical tunneling barriers, Teague in his thesis, "Room Temperature Gold-Vacuum-Gold Tunneling Experiments" (North Texas State University, Denton, Texas, 1978, available from University Microfilms) incorporated herein by reference, proposes adjusting thin-film microbridges using the surface strain

developed in a piezo-electric crystal. Break junctions extend this idea to include bulk samples. See, J. Moreland and J. W. Ekin, J. Appl. Phys. 58 (10), Nov. 1985, p. 3888, the whole of which document is being incorporated by reference. This represents a technological break through in that, traditionally, properties measured by tunneling spectroscopy were usually inferred from measurements on thin films of that material. Break junctions, on the other hand, provide a straight forward process for achieving tunneling measurements of freshly exposed bulk materials without oxide barriers or thin film depositions previously required for junction stability.

SUMMARY OF INVENTION

Accordingly, it is an object of the present invention to provide an apparatus capable of creating break junctions for establishing electron tunneling currents across a fracture in a conducting material.

Another object of the present invention is to provide an apparatus capable of creating break junctions without disturbing the chemical nature of the material.

It is a further object of the present invention to provide an apparatus capable of creating break junctions by developing the necessary strain to fracture conducting materials that are in bulk form and are of varying degrees of brittleness.

Other objects and advantages of this invention will become more apparent hereinafter in the specification and drawings.

In accordance with the invention, a substrate is laminated onto a surface of an elastic beam on either end to form a central unattached section. A

conducting material is then mounted over a gap in the central unattached section of the substrate and broken by elongating the surface of the beam to form a break junction for establishing an electron tunneling junction between fracture elements. Breaking the conducting material in an inert environment prevents oxidation of the freshly exposed fracture surfaces. The spacing between the fracture elements can then be adjusted to obtain a tunnel junction by varying the elongation force applied to the beam. Stable low leakage tunneling I-V characteristics can be obtained sufficient for tunneling spectroscopy of the conductor. In addition, once tunneling is established, the addition of chemically active impurities to the inert environment can be detected as they react with the surfaces of the fracture elements.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of the laminated substrate assembly before the conducting material is applied to the assembly.

Fig. 2 is a cross-sectional view of the beam bending configuration according to the present invention before fracture.

Fig. 3 is a cross-sectional view of the three point bending beam configuration according to the present invention after the fracture.

Fig. 4 is an exploded view of area A shown in Fig. 3.

Fig. 5 is a set of I-V curves for a Nb-Sn break junction immersed in liquid helium.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now more particularly to the preferred embodiment of the invention selected for illustration, Fig. 1 shows the long side of the laminated substrate assembly designated generally by 10 used to break a conducting material. A glass cover slip 14 and a glass microscope slide 12 are attached at two sections designated by sections g, using an adhesive 16 such as an acrylonitrile adhesive. The two sections g are thereby separated by a central unattached section 15. As representative examples, the glass microscope slide 12 and cover slip 14 may each be 7 mm wide and 13 mm long. The cover slip 14 is typically 0.2 mm thick. The length of sections g are each typically 5 mm. After the adhesive 16 has cured, the cover slip 14 is scribed and broken by bending the laminated substrate assembly 10 leaving a well defined substrate fracture 22. The fracture may, for example, be on the order of 0.2 mm deep and nominally 0.25 - 0.3 mm wide along the surface of the laminated substrate assembly 10.

Conducting material in the form of filaments 18 are mounted across the substrate fracture 22 thereby forming a free central section 23 of the filaments 18 over the substrate fracture 22 as shown in Fig. 2. The filaments 18 are fixed to each side of the laminated substrate assembly 10 with silver paint 20 thereby providing a bending beam geometry designated generally by 11. The silver paint 20 also provides electrical contact with the filaments 18. The cover slip 14 is broken before mounting the filaments 18 in order to relieve internal stress acquired when the cover slip 14 was glued to the slide 12. The bending beam geometry 11 is then mounted in an iron electromagnetic bender that

applies forces as shown in Fig. 3. See, for example, J. Moreland et al Rev. Sci. Instrum., 55, 399 (1984), incorporated herein by reference.

Referring now to Figs. 1 and 4 in which Fig. 4 shows an exploded view of area A of Fig. 3, the central unattached section 15 serves to concentrate the bending strain of the substrate assembly 10 near the fracture 22 in the cover slip 14. In this way the local strain at the fracture 22 can exceed the elongation strain at which the filaments 18 fracture thereby forming break junction 24 before the laminated substrate assembly 10 fractures. Referring now to Fig. 2, if the length of the central unattached section 15 of the cover slip 14 is s and the length of filament 18 along the free central section 23 is d , then the strain concentration factor is $e = s/d$. When $s = 3$ mm and $d = 0.3$ mm then $e = 10$. Brittle materials typically fracture at around a 1% strain. Therefore, with a concentration factor of 10, the bending beam geometry 11 just described only requires a 0.1% surface strain developed by the bending force in order to fracture the filaments 18. Typically, this corresponds to a force of about 100 N for the given geometry. It is important to remain below the elastic limit of the glass slide 12 or else the fracture may not collapse into a tunnel junction 24 when the bending force is decreased. Furthermore, since the stiffness of glass requires strong bending forces, the effects of outside vibrations, which are relatively small compared to the applied forces, are lessened. However, other materials exhibiting these same qualities may also be used effectively for both slide 12 and cover slip 14. These materials could also be conducting materials as long as the slide 12 and the

cover slip 14 were electrically isolated from the filaments 18.

In operation, the bending beam assembly 11 is mounted on the end of a probe designed for experiments in a liquid helium storage Dewar. Once the assembly 11 is immersed in liquid helium, the filament 18 is broken by slowly increasing the force applied to assembly 11. The force is then decreased bringing the two broken ends of filament 18 towards each other until a tunneling current can be seen in the I-V trace on an oscilloscope. Thus, the bending beam assembly 11 allows for the mechanical adjustment of break junction 24.

Operation in liquid helium minimizes the effect of thermal fluctuations on the mechanical stability of break junctions 24 since thermal expansivities become vanishingly small at temperatures approaching absolute zero. Also liquid helium provides some fluid damping. In addition, breaking the filament 18 in liquid helium prevents contamination of the freshly exposed fracture surface. However, the bending beam assembly 11 will also effectively form a break junction 24 in a vacuum, gas or other fluid as long as vibrations and surface contamination can be otherwise controlled. Optimum conditions could result in break junction sensitivities to the relative displacements of the fracture elements of better than one picometer.

Many materials can be manufactured in filamentary form. Nb-Sn filaments from magnet wire, for example, are easily adapted to break junctions since the elongation and strength of Nb-Sn are such that the filaments snap before the laminated substrate exceeds its elastic limit or before the filaments 18 slip.

Fig. 5 shows I-V curves that demonstrate the tunneling nature of a Nb-Sn break junction formed in liquid helium at 4°K. As the electromagnet current applied to the glass slide increases, the bending force and the surface strain of the glass slide increase, thereby increasing the width of the break junction and decreasing the normal conductance of the junction. As can be seen in Fig. 5, the normal conductance decreases exponentially with an estimated increase in the surface strain of the glass beam. In addition, the marked features of very little current flow at low voltages (referred to as a tunneling energy gap) in each of the curves are classic signatures of electron tunneling in a superconducting tunnel junction. These features can be used to determine the superconducting energy gap of this particular Nb-Sn filament (10 mV) and demonstrate the spectroscopy capabilities of the break junction method.

The dimensions given for the substrate assembly 10 are for purposes of illustration only. Dimensions will vary according to the materials used in the substrate assembly 10 as well as the conducting material to be broken. For example, a longer substrate assembly 10 could be used to develop more strain for a given force if a conducting material has a high elongation. Other alternatives include replacing the silver paint contacts with stronger attachment materials such as cryogenic epoxies for samples with a high ultimate strength. Another possibility would be to break thin films evaporated directly onto laminated substrate assemblies.

Thus, although the invention has been described relative to specific embodiments thereof, it is not so limited and numerous variations and

modifications thereof will be readily apparent to those skilled in the art in light of the above teaching. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

WHAT IS CLAIMED IS:

1. An apparatus for mechanically forming break junctions for establishing an electron tunneling current across a fracture in a conducting material comprising:

a beam;

a substrate fixably laminated to a surface of said beam at portions thereof and having a central unattached section of said substrate between said beam and said substrate and wherein a substrate gap is formed in said substrate along said central unattached section;

a conducting material mounted across said substrate gap and fixed to said substrate on both sides of said substrate gap wherein a free central section is formed over said substrate gap and wherein a break junction is formed in said material along said free central section wherein said central unattached section serves to concentrate the strain developed at the surface of said beam to exceed an elongation strain of said conducting material at fracture of said conducting material when the surface of the beam is elongated.

2. An apparatus as claimed in claim 1, wherein said beam is made of an elastic material.

3. An apparatus as claimed in claim 2, wherein said elastic material is glass.

4. An apparatus as claimed in claim 1, wherein said substrate is glass.

5. An apparatus as claimed in claim 1,

wherein said substrate is fixably laminated to said beam at said ends of said beam using an adhesive.

6. An apparatus as claimed in claim 1, wherein said conducting material is fixed to said substrate with an adhesive.

7. An apparatus as claimed in Claim 6, wherein said adhesive is silver paint.

8. An apparatus as claimed in claim 1, wherein said beam apparatus is completely immersed in an inert environment before elongation of the surface of said beam.

9. An apparatus as claimed in claim 8, wherein said inert environment is liquid helium.

10. A method for mechanically forming break junctions for establishing an electron tunneling current across a fracture in a conducting material comprises the steps of:

- a) providing a beam;
- b) fixably laminating a substrate to a surface of the beam at portions thereof forming a laminated assembly having a central unattached section of said substrate between the beam and the substrate;
- c) forming a gap in said substrate along said central unattached section;
- d) mounting a conducting material across the substrate gap;
- e) fixably adhering the conducting material to both sides of the substrate gap wherein a free central section of said conducting material is formed over the substrate gap; and

f) elongating the laminated assembly with the conducting material fixably adhered thereto until a fracture is formed along said free central section of said conducting material.

11. A method as claimed in claim 10, further including the step of immersing the laminated assembly with the conducting material fixably adhered thereto in an inert environment after said step of fixably adhering the conducting material and prior to said step of elongation.

12. A method as claimed in claim 13, wherein the inert environment is liquid helium.

13. A method as claimed in claim 10, further including the step of adjusting the fracture until an electron tunneling current is established across the fracture along said free central section.

14. A method as claimed in claim 11, further including the step of adjusting the fracture until an electron tunneling current is established across the fracture along said free central section.

15. A method as claimed in claim 10, wherein the central unattached section serves to concentrate the strain developed at the surface of the beam to exceed an elongation strain of the conducting material at fracture of the conducting material when said step of elongation as defined in step g) occurs.

16. An apparatus for mechanically forming break junctions for establishing an electron tunneling current across a fracture in a conducting material comprising:

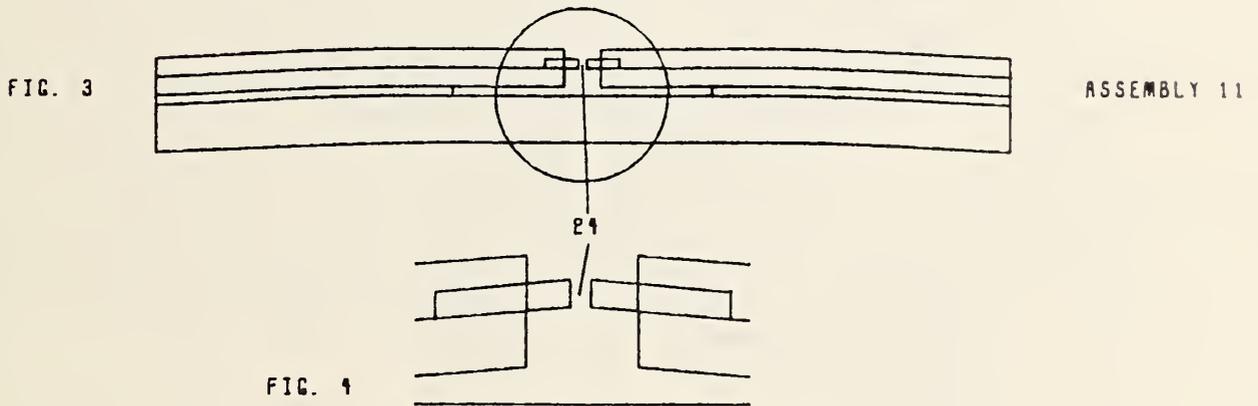
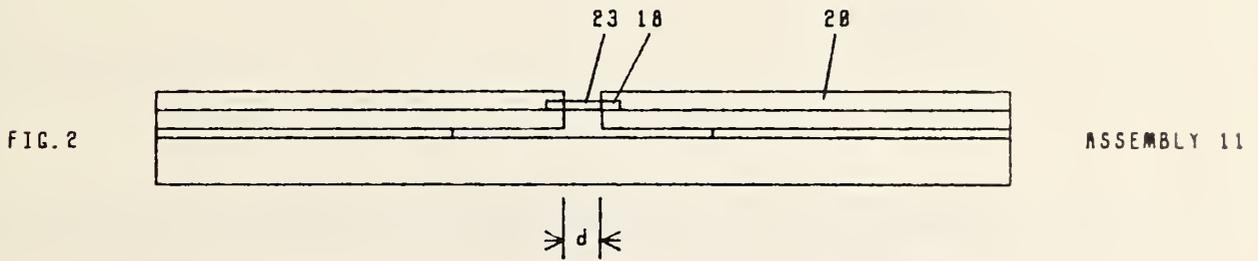
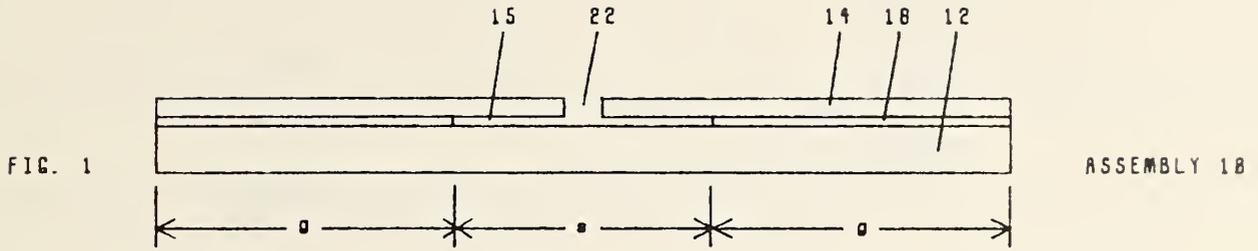
a beam;

a substrate fixably laminated to a surface of said beam at portions thereof and having a central unattached section of said substrate between said beam and said substrate and wherein a substrate gap is formed in said substrate along said central unattached section by bending said substrate; and

a conducting material mounted across said substrate gap and fixed to said substrate on both sides of said substrate gap wherein a free central section is formed over said substrate gap and wherein a break junction is formed in said material along said free central section during the bending of said beam.

ABSTRACT OF THE DISCLOSURE

A method and apparatus for forming mechanically adjustable break junctions for establishing an electron tunneling current across a fracture in a conducting material. A substrate is laminated onto an elastic beam on either end thereby forming a central unattached section. The substrate has a gap along the central unattached section. A conducting material is mounted onto the substrate to form a beam assembly. The beam assembly is elongated to form a fracture in the conducting material whereby the central unattached section concentrates the strain near the gap in the substrate. The assembly is then mechanically adjusted until an electron tunneling junction between the fracture elements is developed. Prevention of any oxidation of the freshly exposed fracture surfaces is accomplished by breaking the conducting material in an inert environment.



Nb-Sn/liquid helium/Nb-Sn
T = 4 K

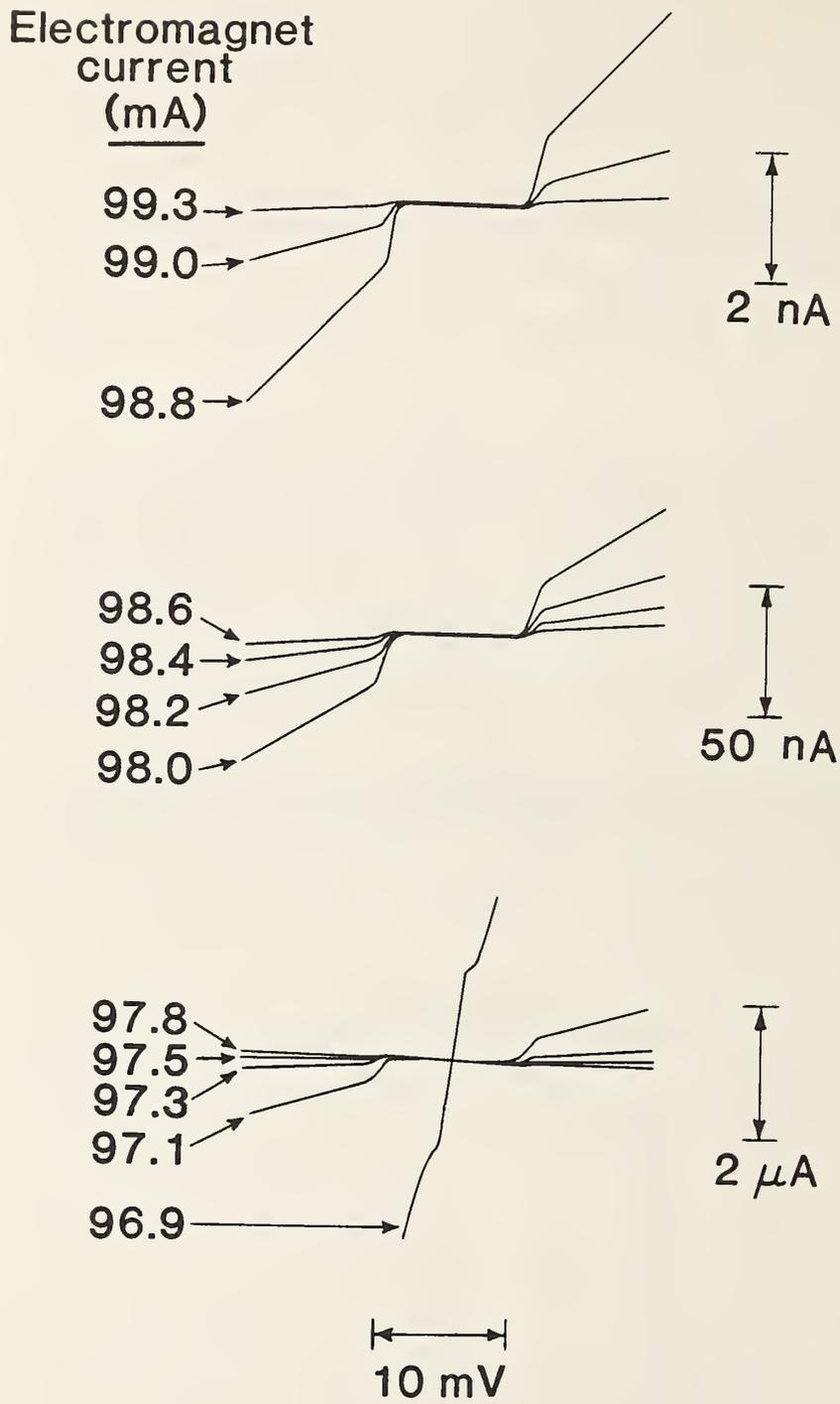


Fig. 5

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET <i>(See instructions)</i>	1. PUBLICATION OR REPORT NO. NBSIR 88-3090	2. Performing Organ. Report No.	3. Publication Date May 1988
4. TITLE AND SUBTITLE <p style="text-align: center;">BREAK JUNCTIONS I</p>			
5. AUTHOR(S) John Moreland, L. F. Goodrich, J. W. Ekin, T. E. Capobianco, and A. F. Clark			
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10. SUPPLEMENTARY NOTES <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
11. ABSTRACT <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> Measurements of the tunneling current-voltage characteristics of break junctions in conventional superconductors can be used to determine their superconducting energy gap as a function of energy. These results agree with those previously obtained using traditional oxide tunneling barriers. Break junctions in some exotic superconductors, on the other hand, have anomalous current-voltage characteristics compared to BCS predictions. Energy gaps and the Josephson effect measured for the new high T_c materials YBaCuO ($T_c = 93$ K) and LaSrCuO ($T_c = 36$ K) indicate that the samples are inhomogeneous with varying gap functions depending on the location of the tunneling contact within the break junction fracture. Break junction data for these materials are within the strong coupling limits of BCS theory.			
12. KEY WORDS <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> break junctions; electron tunneling; energy gap; high T_c superconductors; LaSrCuO; YBaCuO; $YBa_2Cu_3O_{7-\delta}$			
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